SOME ASPECTS IN THE SURFACE CHEMISTRY OF METALS

by

C.J. HAIGH B.Sc. HONS.

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INTRODUCTORY MEMORANDUM

This thesis has been divided into the following sections:-

Section I : The Dehydration of Ferrous Oxalate Dihydrate.

Section II: Kinetics of the oxidation of Nickel Powders.

Section III : Surface Area Measurements of Nickel Powders.

Section IV : Heat of adsorption Measurements.

Section I is isolated and bears little relation to the work reported in the other sections. It is, however, part of a larger programme of work on the chemistry of metal oxalates undertaken in the Department of Chemistry, University of Tasmania.

Sections II and III are related in that the work described in Section III followed as a direct consequence the results of Section II. The work described in both these sections was commenced under the direct supervision of Dr. J.A. Allen, formerly Senior Lecturer in Physical Chemistry, University of Tasmania.

The choice of a volumetric method and the use of nickel powders in Section II was made because of the following:

(a) A high vacuum apparatus had been constructed for previous work and could be used without serious modification as a volumetric apparatus.

(b) Previous work in the Chemistry Department, University of Tasmania had suggested that nickel powders produced by the thermal decomposition of nickel oxalate would be suitable material for oxidation studies.

Section IV has been subdivided into Parts I and II. Part I describes attempts to design and construct a calorimeter suitable for the measurement of heats of adsorption of gases on finely divided powders. Part II is concerned with actual measurements of heats of adsorption of several gases on nickel oxide. The work described in this section was undertaken without direct supervision and all glass construction work, described in this section, has been done by the author.

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SECTION I.

SECTION I

THE DEHYDRATION OF FERROUS OXALATE DIHYDRATE

INTRODUCTION:-

The equilibrium water vapour pressure of the system

$$Ni\ C_2\ O_4 \cdot 2H_2O \rightleftharpoons Ni\ C_2\ O_4 + 2H_2O$$

had been investigated previously ( ) in the Chemistry Department, University of Tasmania. It was desired to extend this investigation to include the equilibrium vapour pressure of the system

$$Fe\ C_2\ O_4 \cdot 2H_2O \rightleftharpoons Fe\ C_2\ O_4 + 2H_2O$$

at a series of temperatures.

EXPERIMENTAL:

(a) Reagents:- Stock solutions of strength 0.5N. were prepared from analytical grade potassium oxalate and ferrous ammonium sulphate respectively. Equal volumes of the solutions at 25°C. were mixed and the ferrous oxalate dihydrate allowed to precipitate overnight. The precipitate was washed free from extraneous ions, dried in an air oven at 60°C. and stored in a desiccator.

(b) Apparatus:- The apparatus used to measure the equilibrium water vapour pressure is shown in fig. 1. It was originally designed as a differential tensiometer for comparing the vapour pressure of nickel oxalate dihydrate with that of another salt hydrate with a known vapour pressure curve. No salt hydrate with suitable characteristics (high temperature of dihydration and high heat of dissociation) could be found and the measurements were made absolutely against vacuum.

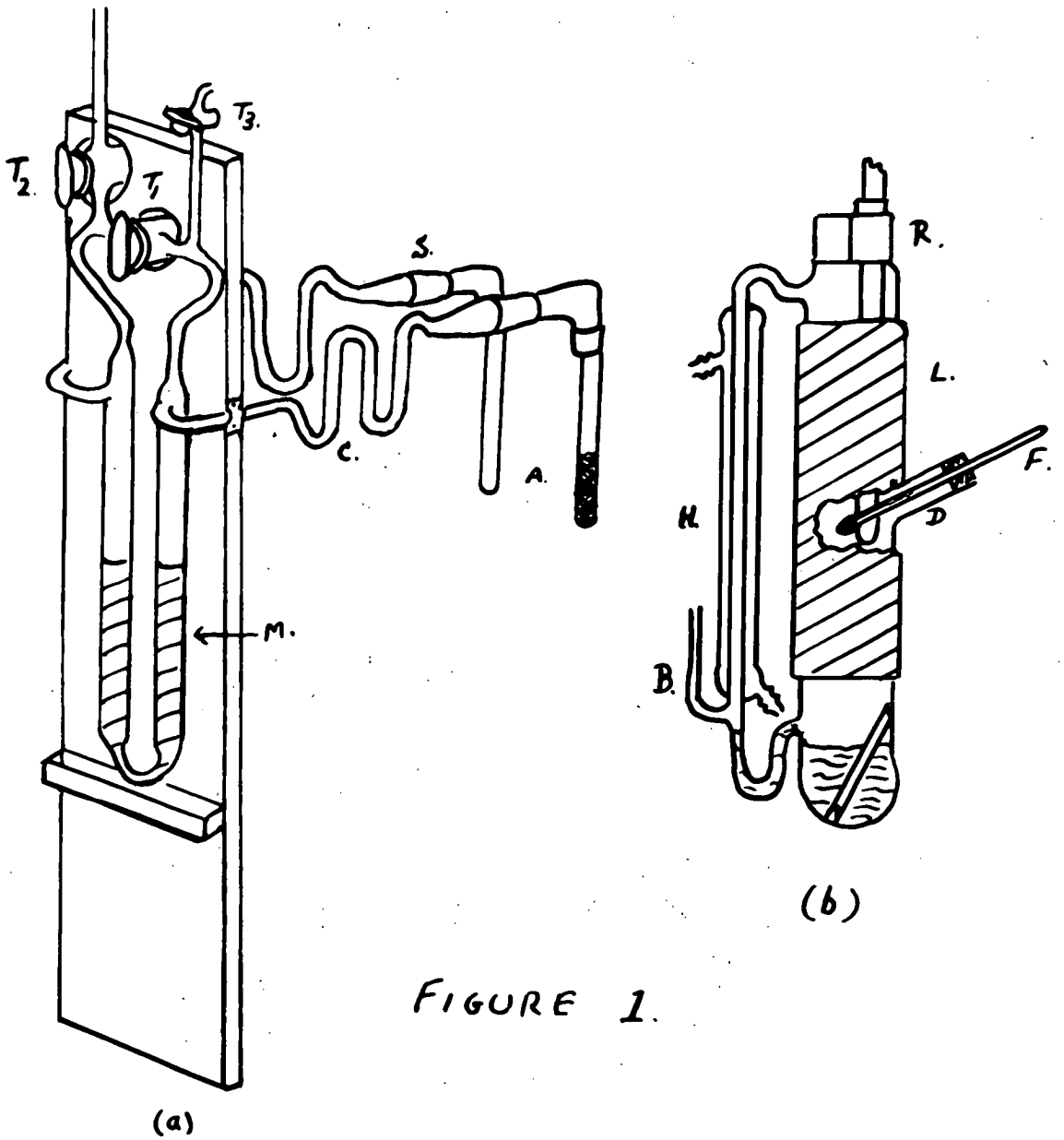


FIGURE 1.

The apparatus in this form worked well for nickel oxalate (1) and was, therefore, used as such for the ferrous oxalate investigation.

The apparatus consisted of a manometer (M) containing di butyl phthalate (S.G. 1.0465 at 19°C.) freed from volatile impurities by heating in vacuum at 200°C. Each limb of the U tube was connected through a flexible glass tubing coil (C) through a cone and socket (S) to an L shaped tube (A). The ferrous oxalate dihydrate was placed in the right hand tube and the left hand tube was continuously evacuated through Tap T_2. A Tap T_1 connected the two limbs of the manometer. The system could be opened to the air through Tap T_3.

The two L shaped tubes fitted into rubber sleeves (R) on the vapour bath, fig.(1b). This was lagged with asbestos tape (L) and the thermometer (E) fitted into the side arm (D) and was level with the bottom of the tubes (A). A return condenser (H) was let into the side of the vapour bath, which was of all glass construction. A breather tube (B) ensured that the liquid in the bath boiled at atmospheric pressure. The cones and sockets were sealed with apiezon W black wax and were shielded from the heat of the burner by an asbestos sheet.

The liquids used in the vapour bath are listed below. Apart from initial fluctuations the boiling points, although

different from the literature values due to partial decomposition of the organic liquids, remained constant during the measurements.

Table I

Liquid	Boiling Pt. ^{o} C.	Liquid	B. Pt.^{o} C.
N-Butyl Formate	105	Ethyl Carbonate	125
Toluene	110	Ethylene Chloro Hydrin	127
N-Amyl Alcohol	115	Iso-Amyl Acetate	131
Acetic Acid	116.5	Cyclo Hexane	144.

(c) Procedure:- The dihydrate was placed in the right hand tube and loosely packed with glass beads to ensure uniform heating and to facilitate out-gassing. If this precaution was not taken the dihydrate, during the out-gassing, blew up the tube and into the coils. As a further precaution against material entering the coils and possibly the manometer, the top of the tube was loosely packed with glass wool.

With the appropriate liquid in the bath, the tubes were slipped into the sleeves and the cones and sockets sealed. The apparatus was then evacuated for 10-15 hours with Tap T_1 open, the sample being heated a number of times for short periods to remove adsorbed gas. The vapour bath was then heated until the liquid was distilling freely in the condenser. Tap T_1 was then closed and a plot of manometer reading against time was made. The equilibrium showed up as a flattening out of this curve. The heater was turned off, Tap T_1 opened and the whole system evacuated for thirty minutes. The heater was turned on again,

Tap T_1 closed and a second reading of the equilibrium obtained.

The procedure was repeated until the charge of the dihydrate had become exhausted. The first equilibrium pressure was a little high, presumably due to adsorbed gas. The second and third measurements were readily reproducible with a fresh charge of dihydrate.

At the highest temperatures studied, after the first two or three measurements, decomposition of the salt was sufficient to render equilibrium measurements impossible.

Because the manometer was at room temperature measurements could only be carried out up to the saturated vapour pressure of water at room temperature.

The possiblity of correcting the pressure read at room temperature for themomolecular flow was investigated. This correction is zero in the pressure range studied (2) if the glass wool does not act as a porous plug.

Comparative blank tests with and without the glass wool showed that no correction had to be applied.

RESULTS:

The average results over a minimum of three independent measurements at each temperature are shown in Table II.

TABLE II

Temp. °C.	Press. P.mm.Hg.	$10^3/T^\circ K.$	$\log_{10} P.$
105.0	3.13 ± 0.1	2.644	0.495
110.0	3.98 ± 0.1	2.609	0.599
115.0	5.10 ± 0.05	2.576	0.707
116.5	5.40 ± 0.05	2.566	0.733
125.0	8.11 ± 0.1	2.511	0.909
127.0	8.81 ± 0.1	2.499	0.945
131.0	10.74 ± 0.1	2.474	1.030.

The results tabulated above were plotted in Fig. (2) where $\log_{10} P.mm.Hg.$ is plotted against the reciprocal of the absolute temperature.

The equilibrium vapour pressure over the temperature range investigated is expressed by the equation -

$$\log \underset{mm.Hg.}{P.} = -\frac{3103}{T} + 8.690 \text{ - - - - - - - - - - (1)}$$

from which the heat of dehydration is 14,200 cals./mole.

DISCUSSION

The high heat of dehydration is comparable with the value of 14,050 cals./mole found for the dehydration of nickel oxalate dihydrate (1). This is interpreted to mean that the water molecules are associated with the oxalate groups, possibly through hydrogen bonding.

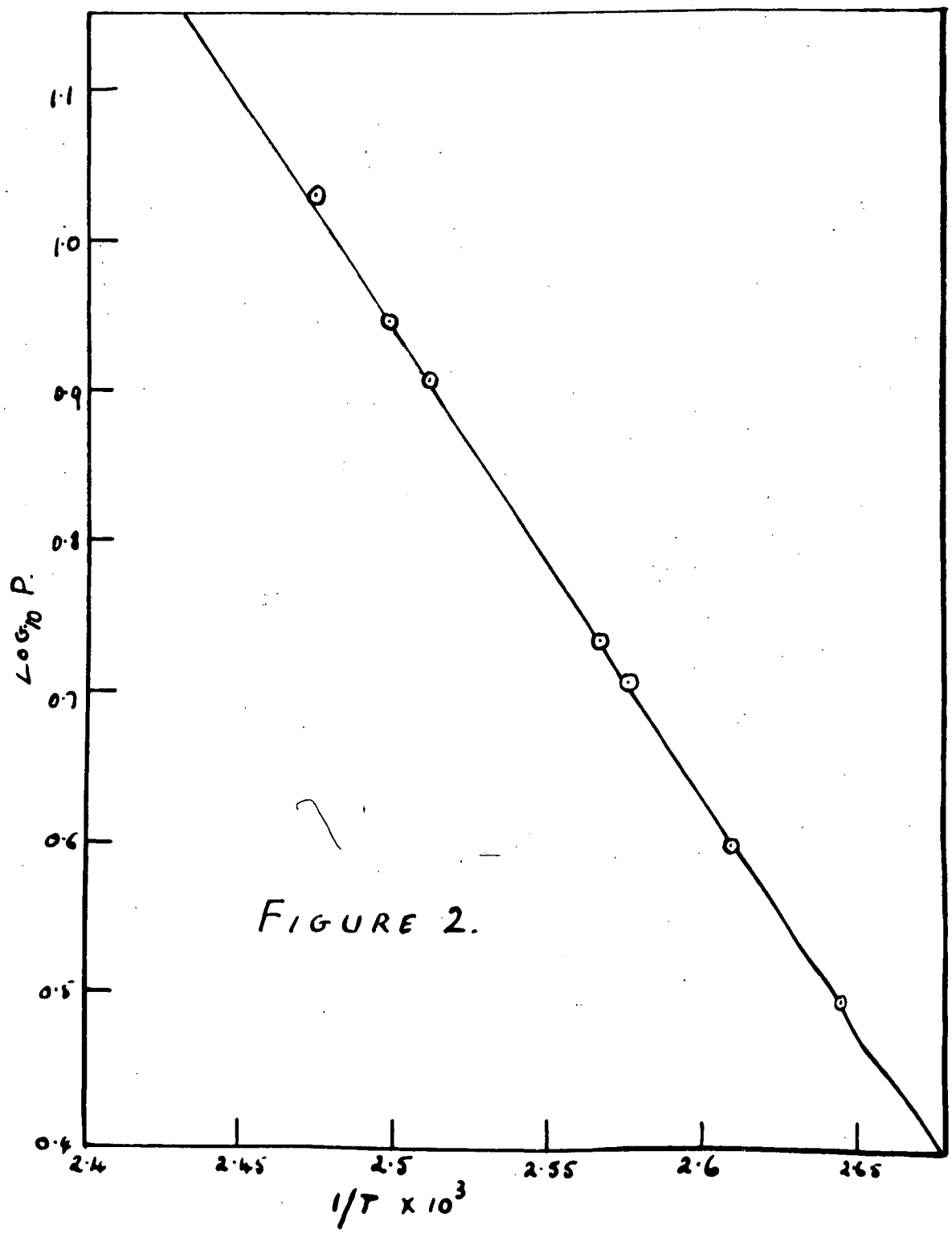


FIGURE 2.

PREPARATION OF ANHYDROUS FERROUS OXALATE

INTRODUCTION:

It can readily be shown that some decomposition (apart from dehydration) takes place when ferrous oxalate dihydrate is heated for several days at temperatures greater than 105°C. The colour of the sample changes from yellow to brown, presumably due to the formation of iron oxides. If it is assumed that equation (1) holds for temperatures lower than the temperature range over which measurements were made, then the calculated vapour pressure at 87°C. is less than 1 mm.Hg. It was decided, therefore, to conduct a vacuum dehydration at 87°C. on the dihydrate in the hope of preparing anhydrous ferrous oxalate.

EXPERIMENTAL -

(a) Apparatus:- The vacuum pistol was of the usual design (3) containing phosphorus pentoxide as the dehydrating agent. The pistol was connected to a "Cenco Hyvac" rotary oil pump via a liquid air trap.

(b) Procedure:- Ferrous oxalate dihydrate was weighed directly from the desiccator into a weighing bottle and then placed in the vacuum pistol. A 70-30% mixture of n-propyl alcohol and water was heated to give a vapour temperature of 87°C. The salt was continously evacuated at 87°C. for several days until constant weight was obtained. This weight, was, however, greater than that corresponding to anhydrous ferrous oxalate and was presumably due to traces of water which could not be removed at that temperature. If any decomposition

of the oxalate had taken place then the final weight would have been less than that corresponding to anhydrous ferrous oxalate.

The procedure was repeated at 95°C. and again constant weight obtained. However, this weight was, within experimental error, identical with that expected for anhydrous ferrous oxalate.

(c) Analysis:- Ferrous oxalate dihydrate and the product formed by dehydration of the salt at 95°C. were analysed for ferrous iron and oxalate composition. The details of the analytical procedure are given in an appendix to this section.

RESULTS:

Table 3 gives the average results of four independent analyses on both the dihydrate and anhydrous salts.

Table III

Ferrous Oxalate Dihydrate $Fe\ C_2\ O_4 \cdot 2H_2O$

Percentage Composition

Fe^{++}	$C_2\ O_4''$	H_2O	
31.05	48.93	20.01	Calculated
30.92	48.90	-	Observed

Anhydrous Ferrous Oxalate $Fe\ C_2\ O_4$

Percentage Composition

Fe^{++}	C_2O_4''	H_2O	
38.82	61.18	-	Calculated
38.80	61.10	-	Observed.

DISCUSSION:

The analytical results are sufficiently close to the theoretical values to state that anhydrous ferrous oxalate can be prepared by vacuum dehydration of the dihydrate at 95°C. The material so prepared is a brownish yellow amorphous solid.

APPENDIX

Ferrous oxalate dihydrate and the product formed by dehydration of the salt at 95°C. were analysed for ferrous iron and oxalate composition by the following procedure.

A weighed sample was dissolved in dilute H_2SO_4 and made up to 250 ml. with boiled out distilled water. An aliquot of this stock solution was evaporated with concentrated H_2SO_4 to decompose the oxalate present. Dilute HCL was added and the iron reduced to the ferrous state by stannous chloride. Mercuric chloride was added to react with the excess $SnCl_2$ and "Zimmerman Rhinehard" solution added. The solution was titrated against $KMnO_4$ standardized against A.R. $Na_2C_2O_4$. This titre gave the total iron present in the sample.

A further aliquot of the stock solution was titrated directly with potassium permanganate at 60°C, thus oxidizing both the ferrous iron and the oxalate present. The latter titre was exactly three times the titre required to oxidize the iron alone, indicating that no decomposition of either the ferrous oxalate dihydrate or the anhydrous material had taken place prior to analysis.

To check this result an aliquot of the stock solution was titrated directly with standard potassium dichromate. It was thought that only the ferrous iron would be oxidized leaving the oxalate unaffected. The results were inconsistent. To test whether this was due to the indicator used (diphenylamine) repeat titrations were followed potentiometrically, using a Mullard magic eye potentiometer titration unit. Saturated calomel and

and a bright platinum electrodes were used throughout. The results were again inconsistent.

In order to prove that the inconsistencies were due to partial oxidation of the oxalate ions, test titrations were done on solutions of ferrous ammonium sulphate containing increasing amounts of oxalic acid. The results are shown in Fig. (3). This clearly indicates that partial oxidation of the oxalic acid takes place, the degree of oxidation being a function of the total oxalate concentration. In addition, the reaction was slow in cold solution, the value of the titre being a function of the time taken to conduct the titration.

Titrations of the stock solutions with potassium permanganate were also followed potentiometrically. The E.M.F. increased steadily up to the point corresponding to the complete oxidation of the ferrous iron. Further additions of the reagent caused a very sharp increase in E.M.F., characteristic of an end point, but on standing this fell to almost the original value. Further addition of potassium permanganate caused gradual increases in E.M.F. until all the oxalate was oxidized. At this point further addition of the reagent caused a large increase in E.M.F., indicating that oxidation was complete.

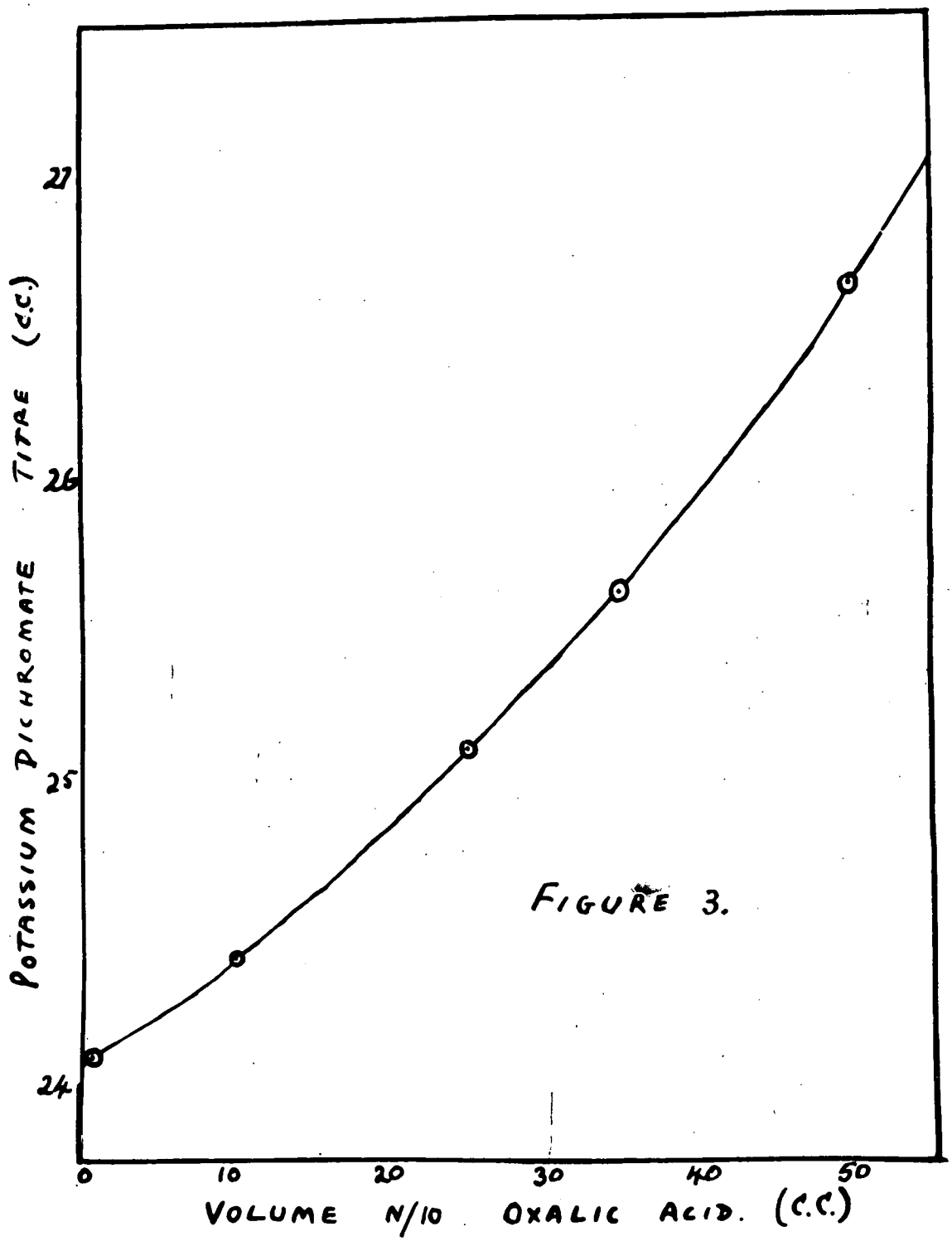

27
26
25
24
POTASSIUM DICHROMATE TITRE (C.C.)
0
10
20
30
40
50
VOLUME N/10 OXALIC ACID. (C.C.)

FIGURE 3.

SECTION II.

SECTION II

KINETICS OF THE OXIDATION OF NICKEL POWDERS

LITERATURE REVIEW:-

In recent years the immense technical uses of metals subject to strong oxidizing conditions has led to considerable research into the extent, rate and possible theories of oxidation of metals. Until 1953 there existed a large mass of uncorrelated literature, but in that year a comprehensive review was published(4).

While it is desirable from the author's point of view to summarise the existing publications, these have been covered so adequately in the above review that no detailed summary will be attempted. Rather, certain ideas and theories which form a background for the present work, together with some recent pertinent publications, will be mentioned.

Several impirical oxidation laws have been found to hold for pure metals. These are most conveniently given in terms of weight increases Δm and time t.

They are -

1. Linear Law:

$$\Delta m = k_1 . t \quad \text{- (1)}$$

where k_1 is a constant.

2. The Power Laws:

$$(\Delta m)^2 = k_p . t \quad \text{- - - - - - - - - - - - - - - (2)}$$ simple parabolic.

$$(\Delta m)^2 = k_p . t + C \quad \text{- - - - - - - - - - - - - (3)}$$ modified parabolic.

$$(\Delta m)^2 + k_a . \Delta m = k_b . t \text{ ---------- (4)} \quad \text{quadratic.}$$

$$(\Delta m)^3 = k_c . t \text{ ---------- (5)} \quad \text{cubic.}$$

Of these the parabolic are the more important.

3. The Logarithmic Laws:

$$\Delta m = k_e . \log. (a.t + 1) \text{ ----------(6)}$$

where a and k_e are constants.

The oxidation time relationships are shown in Fig. (4).

A given metal may follow different equations depending on the conditions. Metals which form protective oxide coatings usually follow some logarithmic plot at low temperatures, but at higher temperatures this usually gives way to one or more of the power laws. Vernon et al (6) have shown, for example, that the oxidation of iron follows the equation -

$\Delta m = k . \log (a.t + 1) + b$ below 200°C. but follows the parabolic equation -

$(\Delta m)^2 = k.t$ above this temperature.

Similarly, copper has been shown to follow logarithmic, cubic and parabolic laws in succession (7) (8), while aluminuim follows a logarithmic law below 300-500°C. (9) (10), but a parabolic law above this temperature.

Various logarithmic equations have been employed to fit experimental data. These may be simple, as found by Vernon et al (11) for zinc, or more complex, as suggested by Lustman and Mehl (12).

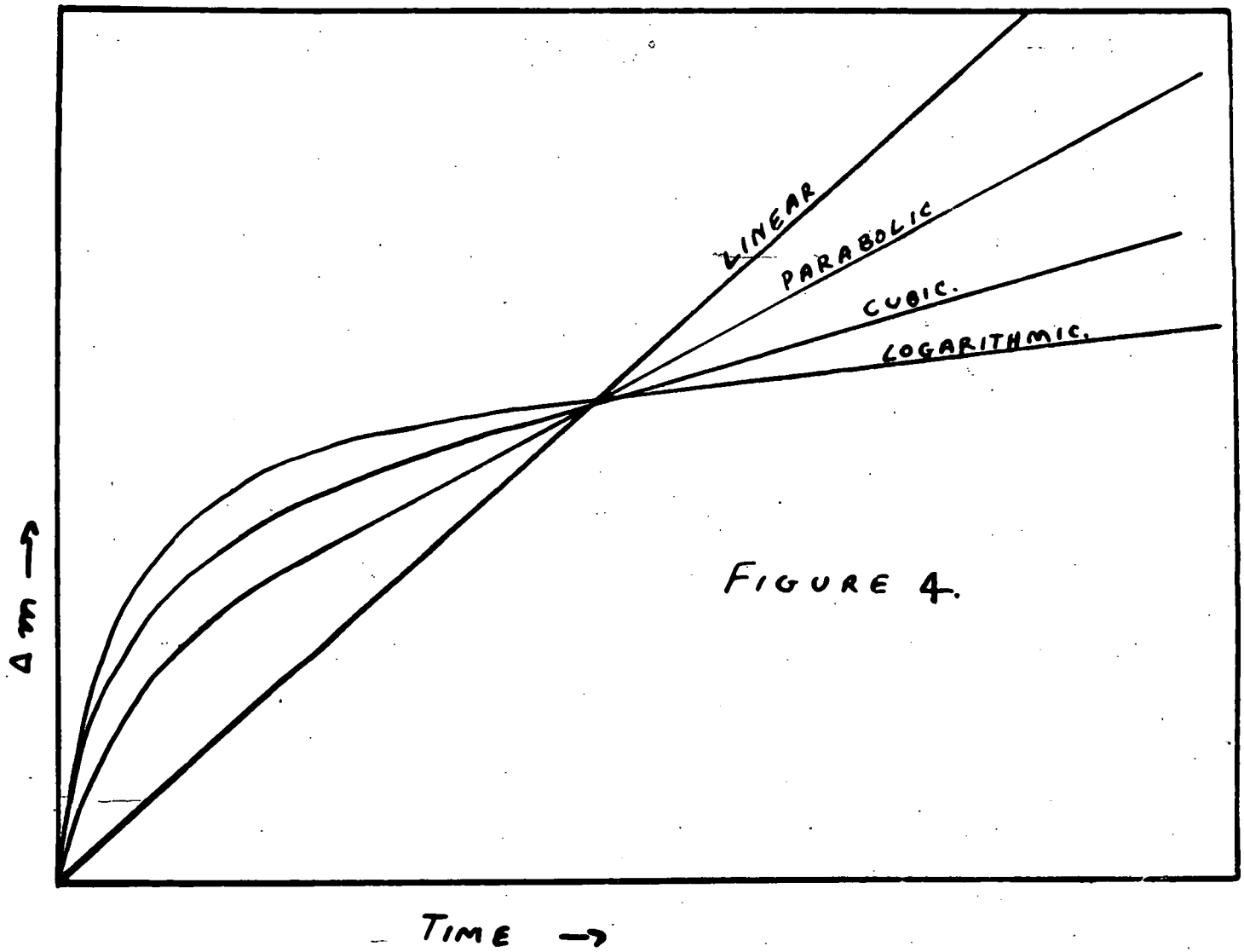


FIGURE 4.

It may be pointed out however, that almost any process which tends to come to a standstill after a while would approximately conform to some kind of logarithmic equation, the degree of fit depending on the number of constants involved in the equation.

There are several factors which play an important part in influencing the type of oxidation law which a given metal will follow. These have been adequately covered elsewhere (4) and will only be briefly mentioned.

One factor involved is the type of compound which the metal can form under the given set of conditions of temperature, pressure and composition of the gas phase. The possible compounds will not only be those that are thermodynamically stable, but also those metastable compounds that have small positive free energies of formation. These must be included because the energy states at the interface differ considerably from those in the bulk material. Thus metallic compounds which are normally unstable in the bulk or standard state may be formed on suitable surfaces. Nickel, for example, forms only one stable oxide Ni O, but $Ni_2 O_3$ may be grown on surfaces of $AL_2 O_3$ and NiO_2 on TiO_2 (13). Wustite FeO is normally unstable below 570°C. but Gulbransen (14) has detected it in films at temperatures as low as 400°C. In this regard it may be noted that the nickel powders used in this investigation are quite different from nickel in its standard state.

The rates of most surface oxidation reactions vary with temperature according to an equation analagous to the Arrhenius equation -

$$k = A\, e^{-Q/RT}$$

where the term activation energy is retained for Q and A is a constant of dimensions depending on the dimensions of k. The equation is applicable to reactions following parabolic (15), linear (16) and logarithmic (17) equations. In some cases there is a break or bend in the graph of log $k \sim \frac{1}{T}$ corresponding to an equation of the form

$$k = A_1\, e^{-Q_1/RT} + A_2\, e^{-Q_2/RT}$$

suggesting that two processes of different activation energies are rate determining in two different temperature ranges. Such is the case in the oxidation of copper (18).

Gulbransen (19) has attempted to apply the Eyring reaction rate theory (20) to oxidation processes and in the case of parabolic oxidation obtained the following equation -

$$k_p = \frac{2kT}{h} \cdot d^2 \cdot e^{\Delta S^{\times}/R} \cdot e^{-\Delta H^{\times}/RT} \qquad \text{----------(7)}$$

where k_p is the parabolic rate constant,

k is the Boltzman constant,

h is Plank's constant

and d is the closest cation distance in the oxide, assuming cation diffusion is the rate determining step.

$\Delta S^{\times}$ and $\Delta H^{\times}$ are the entropy and heat of activation respectively.

Moore (21) has evaluated values for $\Delta S^{\times}$ and $\Delta H^{\times}$ for some pure metals. However, the interpretation of the fluctuations in $\Delta S^{\times}$ is confusing and it is debatable whether this more detailed approach is at present warranted.

The effect of pressure on the rate of oxidation has yielded some information on the mechanism of oxidation (22, 23, 24, 25) but generally speaking the position is confused, especially at low pressures. No satisfactory explanation exists for the "critical pressure" of Wilkins and Rideal (26) (27).

The preparation of surfaces prior to oxidation is of special importance. The effect of contamination of the surface by polishing agents, the influence of annealing temperature and the effect of repeated reduction with hydrogen on the oxidation of metals is well known and is adequately discussed elsewhere (4). The effect of pores, cracks and blisters on oxidation rates has been noted by many workers, but little systematic work on this aspect of the subject has been undertaken because the effects are hard to reproduce.

The texture, structure and orientation of surface films has received considerable attention in recent years. However, the experimental observations are not always in agreement (28)(29). A more detailed investigation in this aspect is required before theoretical and practical results can be correlated.

Disagreement also exists between results on the rate of growth of oxide films on different crystal faces.

Thus Rhodin (30), and Gwathmey and Young (31) have observed different rates on different faces of copper, but Bosinka, Polling and Charlesby (32) do not observe this difference in the case of aluminium. However, no satisfactory correlation of the variation (if any) is possible in the absence of essential data on interfacial energies.

The purity of the metal has been shown to have a pronounced effect on the oxidation rates.

Kubaschewsky and Von Goldbeck (33), in reviewing the publications on the oxidation of nickel, note a difference of one power of ten in the oxidation rates, the less pure qualities giving the higher rates. They suggest that manganese and to a lesser extent iron as impurities are responsible for decreasing the resistance to oxidation. Wagner and Zimens (34) have altered the oxidation rate of nickel by adding impurities of difference valence. Such experiments have verified the prediction of Wagner, for metals forming layers of metal deficit semi-conductors.

On the other hand, the mechanism involved in the oxidation of zinc is the reverse of that of nickel. Hauffe (35) has predicted and observed that high purity zinc is oxidized faster than material of lower quality. Generally speaking impurities that are chemically similar to the base metal have a smaller effect than chemically different impurities. These latter impurities, even in small amounts, may have a pronounced effect.

The theoretical position, with regard to the oxidation laws, is far from complete.

The parabolic law to which most metals conform at high temperatures has been accounted for by the Wagner theory (36). At low temperatures the Mott Cabrera theory (37) has been partially successful, but in some respects has been shown to be incorrect (38). At intermediate temperatures different metals obey various rate equations but no comprehensive theory exists for this temperature range. Some aspects of the major theories will be briefly discussed, but no detailed summary has been attempted.

WAGNER'S THEORY

Wagner's theory (36)(39) of oxidation of metals is confined to surface reactions that obey the parabolic time law, and for which consequently a true diffusion process of ions in the oxide lattice is rate determining. The theory, summaries of which are given in several papers (40)(41) (42), is based on the model of ionic and semi-conductors, which is discussed at length in the review previously mentioned (4). Wagner derived rate equations involving known or measurable quantities (transport numbers, decreases in free energy etc.) and was able to calculate rate constants. The agreement between the calculated and observed results is excellent (4), indicating the essential correctness of the Wagner model. In recent years the basic Wagner theory has been extended and improved, the

most notable contributions being those of Hauffe (43) and Grimley (44). Radio tracer studies have recently provided further confirmation of the Wagner model (45). Various experiments have been conducted to test the validity of the theory by adding impurities of different valence to that of the base metal and observing the change in the rate of oxidation. Without exception the results have been in agreement with the theoretical predictions (46)(47)(48).

THE MOTT CABRERA THEORY

It has been shown experimentally, that many metals when exposed to oxygen or air at room temperature oxidize very rapidly, but after a few minutes the rate drops to very low values when a film 20-50 Å thick has been formed. The region of thin film formation in which a limiting thickness is not exceeded may extend to higher temperatures. At low temperatures metal oxides, in general are good insulators, and if the film grows as a result of diffusion of metallic ions and electrons, then the Wagner model cannot explain the oxidation at low temperatures. Mott (37)(49) has provided an explanation which accounts for some but not all of the results. Mott suggests that as the ions cannot diffuse through the film at low temperatures, the electrons pass from the metal to the oxygen adsorbed on the surface of the film either by thermionic emmission or more probably by the tunnel effect.

By a development of this idea Mott and Cabrera have qualitatively accounted for the growth up to a limiting thickness. These authors have also extended the theory to consider what happens at somewhat higher temperatures when oxidation laws other than parabolic have been found to hold. Allen (50) summarising published and unpublished work writes "Several aspects of the Mott Cabrera theory were subjected to experimental test:- the limiting thickness critical temperature for growth without limit and saturation pressure were in satisfactory agreement with the theory".

Recently Grimley and Trapnell (51) have suggested corrections to some of the assumptions embodied in the Mott-Cabrera theory. These authors have shown that certain extensions of the Mott theory, to account for the different growth laws found at higher temperatures, are incorrect and have given alternative equations. These modified equations are in better agreement with recently published work (52) (53) than the original Mott equations.

The tunnel effect mechanism proposed by Mott has recently been revived in a new form by Hauffe and Ilschner (54). The work of Schewbles (55) on nickel and Hart (56) on aluminium provide experimental proof of the predictions of Hauffe and Ilschner.

The approach to the problem instigated by Mott certainly deserves attention and further elaboration should

contribute considerably to the full theory of oxidation of metals.

Evans (57) has proposed a general equation when the oxidation rate is controlled purely by movement through the film. Two limiting cases of the general equation exist, the simple parabolic law and the inverse logarithmic law. When other factors such as boundary reactions have partial or complete control, these equations are modified to give the mixed parabolic and rectilinear laws respectively. When the effective area varies with time there are other changes leading to various logarithmic laws. The Evans approach is satisfactory in explaining some of the experimental results but is inadequate in other cases.

We may summarise the present position as follows.

At high temperatures the parabolic law holds for almost all metals. Theoretical arguments, starting from different premises, viz. Wagner and Evans, provide an interpretation of the mechanism.

At low temperatures the Mott Cabrera theory, together with the modified form suggested by Grimley and Trapnell, describe some but not all of the experimental results. The approach by Evans also explains some experimental factors.

At intermediate temperatures some confusion exists.

The Wagner mechanism does not hold and the Mott theory, together with modifications, is inadequate in a number of cases. Evans can account for some results and has even suggested theoretical equations for which there are no experimental results (58). In other cases no satisfactory theoretical explanation exists (59).

Further work, both theoretical and experimental, is required, especially in the moderate temperature range. It was hoped that the results of this investigation, as well as being an addition to the experimental data, would throw some light on the mechanism by which metals are oxidized at moderate temperatures.

EXPERIMENTAL:

1. Reagents

(a) Nickel:-

Reagent grade nickel oxalate dihydrate was decomposed in situ at 330°C. to yield finely divided nickel powders. Previous work had shown that the only other detectable product of decomposition was carbon dioxide (60). The actual procedure used will be described elsewhere.

(b) Oxygen:-

This was was prepared by the thermal decomposition of potassium permanganate. The salt was packed into a long thick walled tube connected to the vacuum system via a liquid air trap. The tube was evacuated for one hour, being gently heated during this time to remove adsorbed gas. Oxygen generation was then commenced until a pressure of 20 cm.Hg. was developed in the system. This flushing gas was then pumped away and generation continued until the storage bulb was filled to a pressure of approximately 70 cms.Hg.

2. Apparatus

A diagram of the apparatus is shown in fig. (6). During the investigation the apparatus was modified considerably. A description of the modified apparatus will be given under a separate heading.

The oxidation apparatus was similar to that used to study the thermal decomposition of nickel oxalate. It

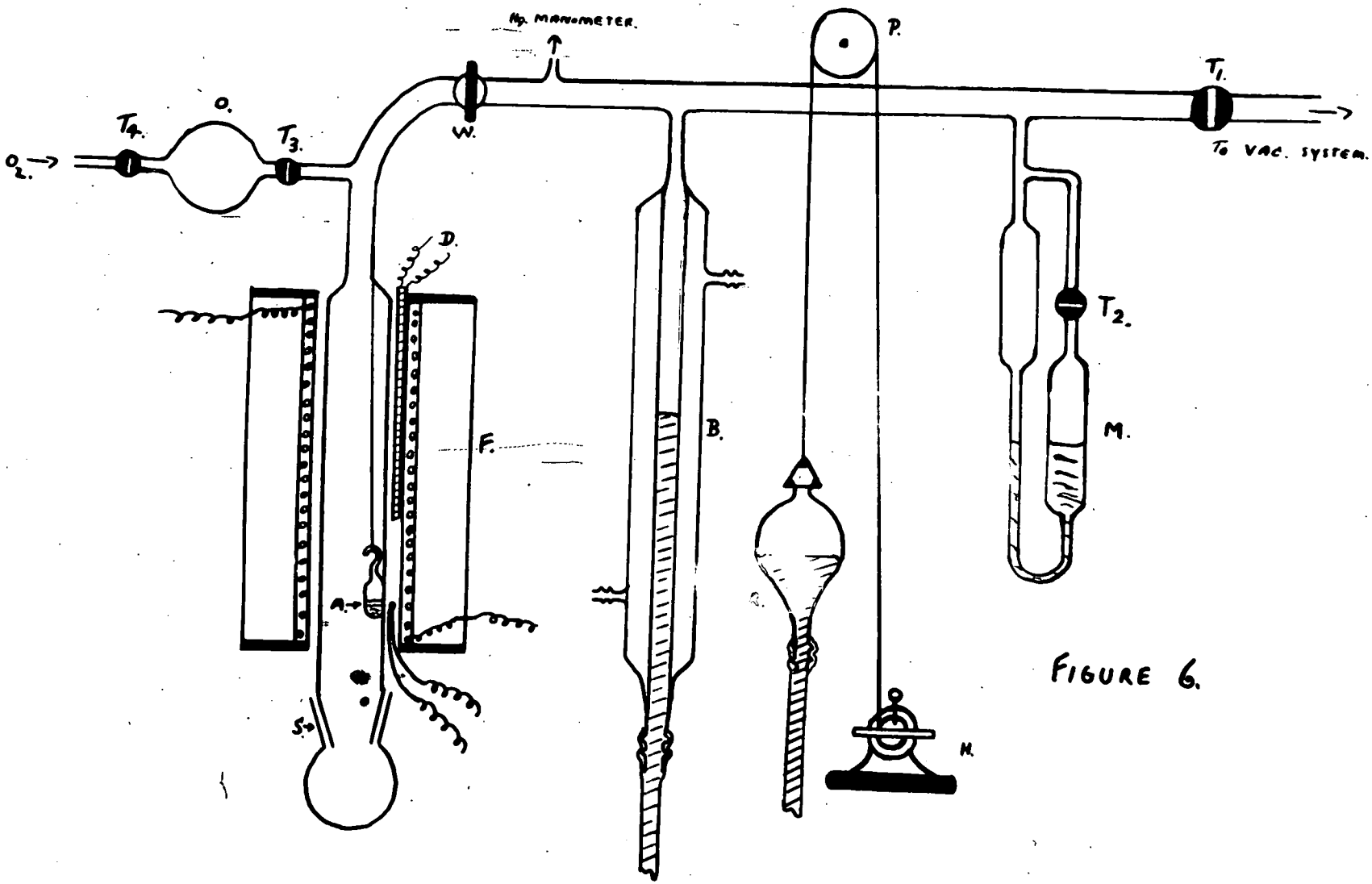


FIGURE 6.

consisted of a wide bore glass tube, the lower end of which was fitted with a cone and socket (S). The upper portion of the tube was surrounded by a ten inch furnace, described under a separate heading. The sample was suspended in a glass ampoule (A) by a thin platinum wire wound round a winch (W) at the top of the chamber.

The volume of oxygen used in an oxidation run was measured at constant pressure by a 0-50 ccs. water jacketted burette (B). The level of mercury in the burette could be varied by means of a mercury reservoir (R) suspended by a cord passing over a pulley (P) to a winch (H) attached to the bench. This winch could be kept in any position by a pin which inserted into any one of a series of holes bored into the winch axis.

The pressure in the system was kept constant by using the levelling device in conjunction with a differential oil manometer (M) containing apeizon oil. The system could be evacuated through tap T_1 by a pumping system consisting of a rotary oil pump, mercury diffusion pump and a trap cooled in liquid air. This system was capable of attaining a vacuum of at least 10^{-5} mm.Hg. A McLeod gauge and a Pirani gauge were also incorporated in the system.

The volume of oxygen admitted to the reaction chamber could be varied by means of a small bulb (O) which could be isolated from the rest of the system by taps T_3 and T_4.

The volume of this bulb was measured before attaching to the system by weighing the volume of mercury it contained. This volume of oxygen at a pressure recorded on a mercury manometer could be expanded into the oxidation apparatus.

The volume of the oxidation apparatus was calculated by allowing a known volume of nitrogen at a measured pressure to expand into the evacuated system, the final pressure being recorded. The volume averaged over ten determinations was 292 ± 1 ccs.

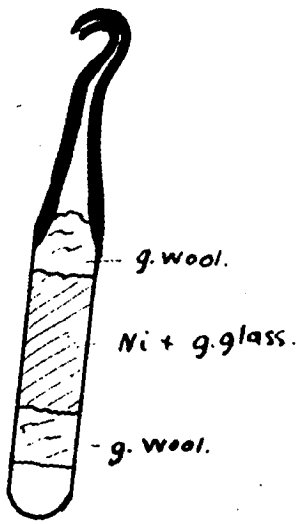
Ampoule Design :

Several different types of ampoules were developed as the work progressed but virtually they remained the same. They consisted of thin walled pyrex tubing drawn down into a strong capillary at one end, which was then bent in the form of a hook. A loose plug of glass wool was packed into this constricted end, the sample weighed into the tube and shaken down towards the constricted end. The walls of the tube were then cleaned with a pipe cleaner and the open end sealed. In later experiments the glass wool was omitted and as a further modification the ampoule size was increased and the bottom face blown flat. Fig. (5) illustrates the ampoules developed.

Furnace Design and Control Unit :

The ten inch furnace (F) (fig.(6)) consisted of a nichrome winding on a wide bore silica tube. In later experiments the silica tube was replaced by a steel tube of

(a)



(b)

(c)

(d)

FIGURE 5.

larger diameter. The furnace could be raised or lowered around the reaction chamber by means of two clamps rigidly attached to the furnace and sliding vertically on a metal bar attached to the framework of the vacuum system.

The temperature of the furnace was controlled by means of a platinum resistance control unit. The platinum resistance wire (D) of 20 Ohms. resistance at room temperature was non inductively wound on a mica strip, protected by two further mica strips and placed in the furnace tube. The control unit was designed and constructed by the Electrical Engineering Department of the University of Tasmania. The operation was satisfactory for several months at a time, but occasionally the unit broke down with drastic results. A Sunvic Control Unit was used in later experiments. With either control unit the temperature inside the furnace could be maintained at $\pm 1^{\circ}$ C. over the range 100-800°C.

The temperature gradient inside the furnace was measured with a thermometer suspended at various heights up a wide bore glass tube placed in the furnace tube. Fig. (7) illustrates the results. At a point about mid-way up the furnace the temperature gradient was less than 1°C. over a length of one inch.

During an oxidation experiment, when the furnace was raised up into position, the ampoule was wound up inside the tube such that it was in that section of the furnace where

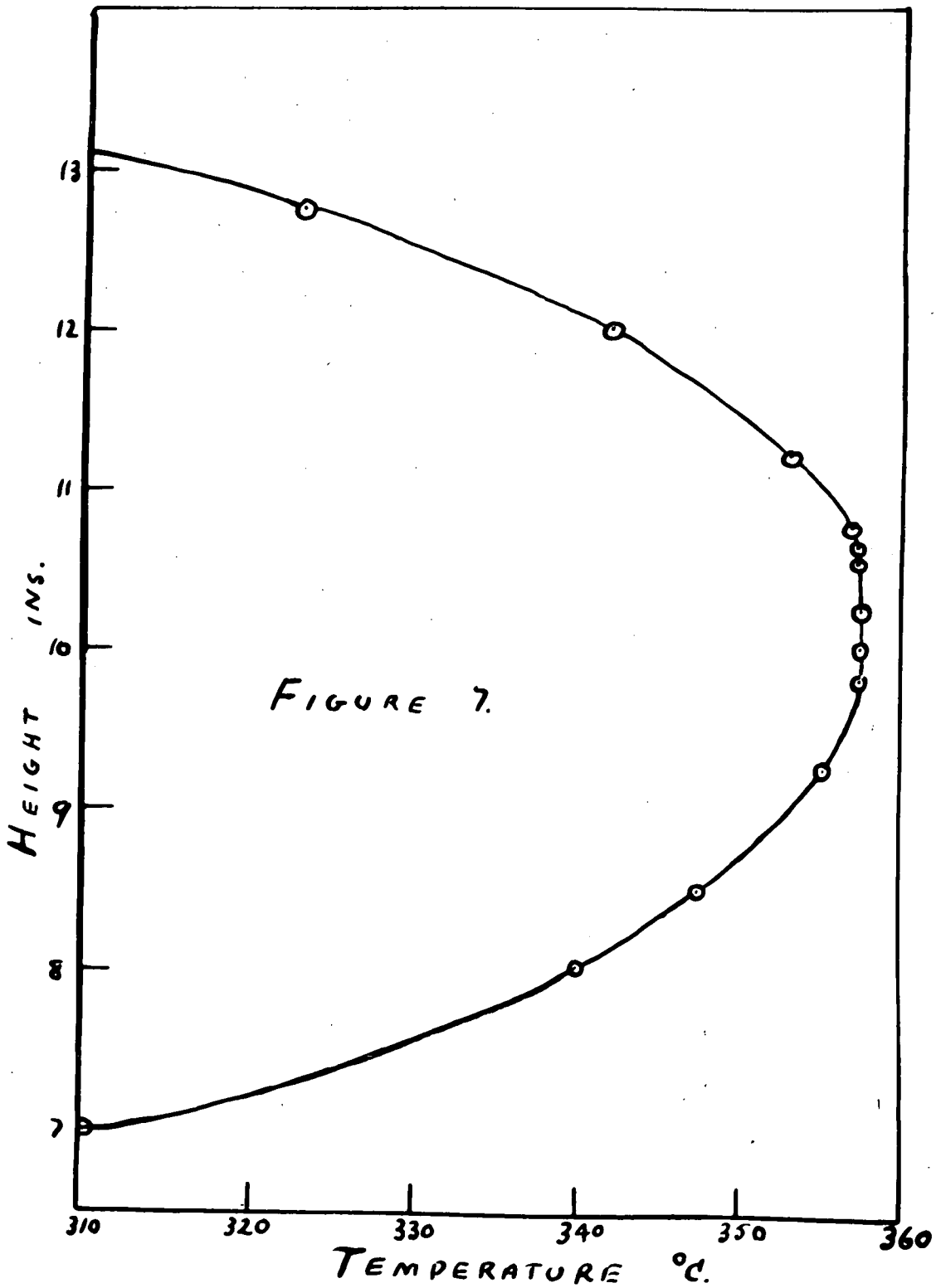

13
12
11
10
9
8
7
HEIGHT INS.
310
320
330
340
350
360
TEMPERATURE °C.

FIGURE 7.

the temperature gradient was least. The temperature at this level was measured by a chromel - p - alumel thermocouple pushed up inside the furnace tube. The thermocouple, with cold junction immersed in a dewar vessel containing crushed ice was connected to a Cambridge Vernier potentiometer.

The E.M.F. could be read to 0.00001 volts. The thermocouple was calibrated against an accurate thermometer, the calibration graph being shown in fig.(8).

Modified Apparatus :

Because of the inconsistency of the results obtained with the apparatus just described it was decided to modify the apparatus and technique. It was desirable to construct an apparatus capable of surface area measurements as well as kinetic work. Therefore the following modified apparatus was constructed.

Fig.(9) illustrates the apparatus. It consisted essentially of a sample bulb (A) of approximately 10 ccs. capacity sealed to the end of a capillary tube. Two burettes B_1 and B_2 were included in the system, B_1 being required for surface area measurements and B_2 replacing the 0-50 ccs. burette used in the kinetic work. Burette B_2 was calibrated before connecting to the system by weighing the volume of mercury contained between marks on a graduated scale attached to the rear face of the burette. The mercury level in the burette could be varied by the winch and pulley system described earlier.

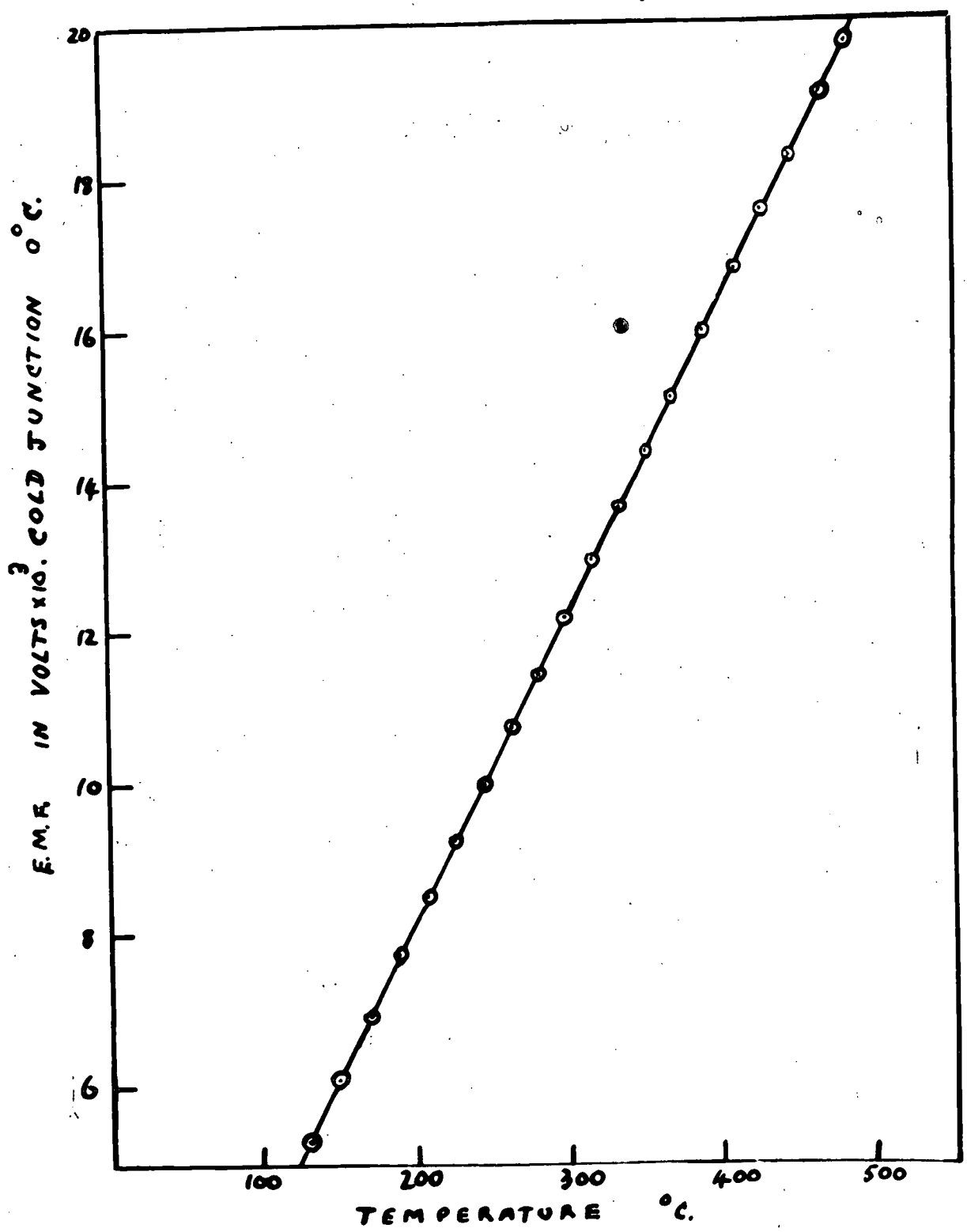

E.M.F. IN VOLTS x 10^3. COLD JUNCTION 0°C.
20
18
16
14
12
10
8
6
100
200
300
400
500
TEMPERATURE °C.

FIGURE 8.

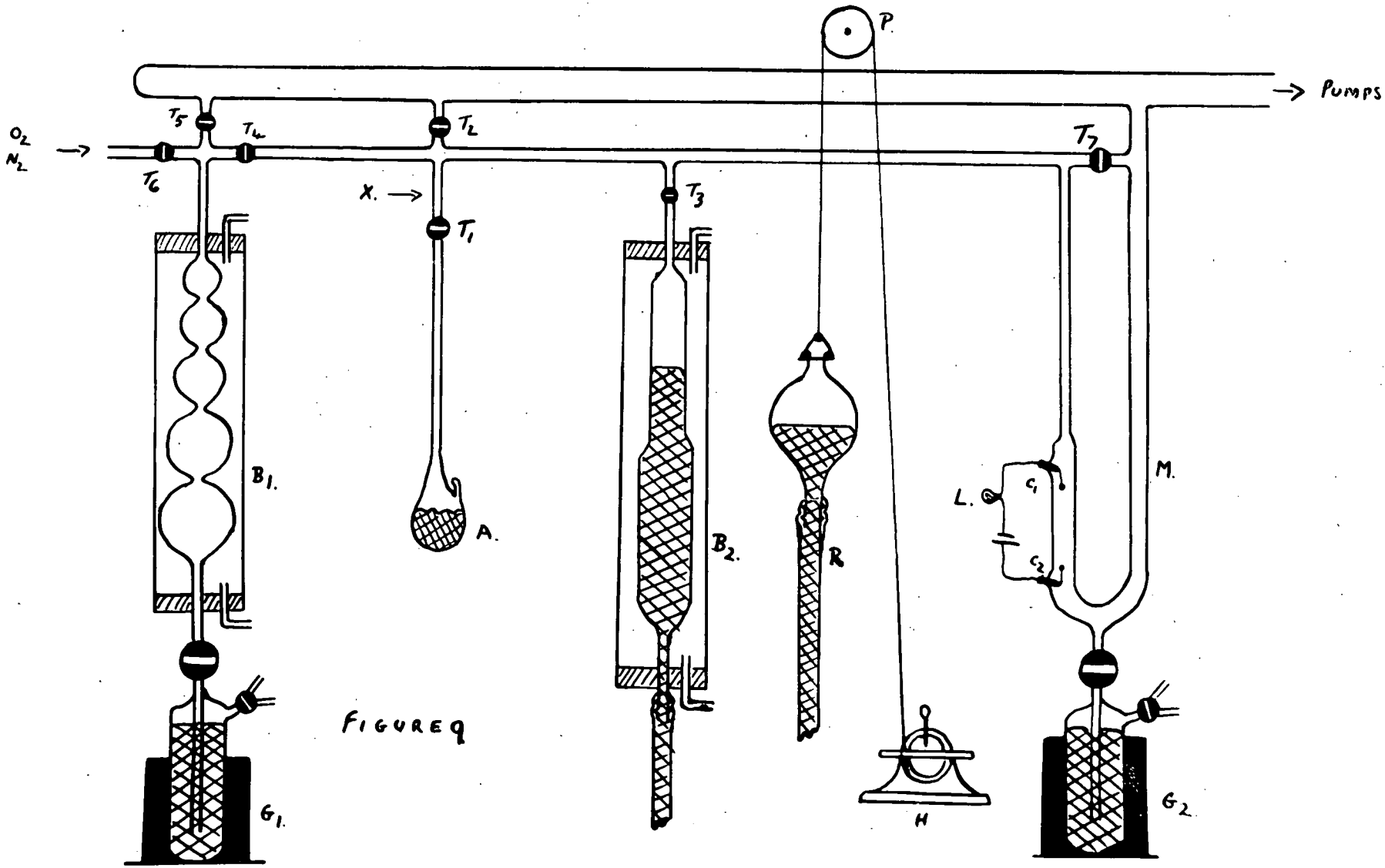


FIGURE 9

The differential oil manometer was replaced by a mercury manometer (M). This manometer, which was designed primarily for surface area measurements, was fitted with two platinum contacts (C_1 and C_2) spot welded on to tungsten seals through the walls of the manometer. These contacts were wired to a 2 volt supply such that when the mercury was in contact with the top platinum wire a small lamp (L) was illuminated.

The volume of mercury in the manometer could be varied from the reservoir (G_2). With such an arrangement the mercury level in the left hand limb of the manometer could be adjusted to exactly the same level each time a pressure reading was made.

The volume of the tubing connecting the burettes and sample bulb was determined as before, by measuring the drop in pressure when nitrogen was allowed to expand into the evacuated system.

Experimental Procedure :

The actual procedure adopted was different for the modified apparatus and therefore will be discussed under a separate sub-heading.

(a) Ampoule Apparatus

The ampoule containing a weighed amount of nickel oxalate ($\simeq 0.05$ gms.) was attached to the platinum wire and wound up into the lower section of tube. The cone and socket were sealed with apiezon grease and the apparatus evacuated

through tap T_1. After outgassing for a minimum of thirty minutes the furnace was placed in position and the control unit adjusted to give a temperature of 210°C. in the middle section of the furnace. This temperature had been shown previously (1) to be suitable for the rapid dehydration of nickel oxalate dihydrate. The ampoule was wound up into the furnace and brought to rest at the point of minimum temperature gradient. This corresponded to eighteen half turns of the winch after the ampoule had passed the bottom edge of the cone and socket.

The temperature was maintained at 210°C. until dehydration was complete, usually about two hours. The temperature was then raised to 330°C. At this temperature decomposition of the nickel oxalate was fairly rapid (60) and was complete in three hours. This was checked by isolating the system and closing tap T_2 of the differential manometer. If the manometer remained stationary for ten minutes the decomposition was judged complete.

The ampoule was then wound down into the cold section of the tube and the furnace switched off. The lower portion of the tube was then immersed in a Dewar vessel containing liquid oxygen. Two hours were allowed to elapse for thermal equilibrium to be established and then oxygen, at a known pressure, was expanded from bulb (O) as slowly as practicable into the oxidation chamber. After waiting another hour the liquid oxygen was removed, the ampoule brought back

to room temperature and the equilibrium oxygen pressure recorded. Since all volumes and pressures were known the volume of oxygen absorbed by the nickel sample was readily calculated.

The oxygen pressure in the system was then adjusted to 5 cms.Hg., this figure being used in all runs. The furnace was placed in position and its temperature controlled to 300°C. The ampoule was wound up into the furnace and the time when the ampoule entered the furnace was noted. The reaction commenced immediately as indicated by a rise in the level of the left hand arm of the differential manometer. The mercury level in the burette was raised a notch or two on the winch until the manometer fell to below its equilibrium level. The time when the manometer level again reached the zero mark was noted and simultaneously the volume reading taken from the burette. The oil manometer could be read to about $\frac{1}{5}$ mm. oil, i.e. about 0.01 mm.Hg. Readings were continued for about one hour, the reaction rate being very slow after this time had elapsed.

(b) Modified Apparatus Procedure

A weighed amount of nickel oxalate dihydrate (4 gms.) was placed in the unsealed bulb (capacity 10 ccs.) attached to the end of a capillary tube. A glass bead was inserted in the capillary entrance thus preventing the powder falling into the capillary. The sides of the bulb were then cleaned and the bulb sealed. The bulb was then righted, the glass bead falling back into the mass of powder and the capillary attached to the apparatus at point X fig.(9). The sample was outgassed

for several hours and then the furnace placed in position so that the bulb was in the zone of minimum temperature gradient. The oxalate was dehydrated at 210°C. for twentyfour hours and then decomposed at 330°C. for a further twentyfour hours. In later experiments, as a result of the surface area measurements, the decomposed samples were sintered at 500°C. for six hours. At the end of this heat treatment the furnace was removed, the bulb allowed to cool and then immersed in a dewar of liquid oxygen.

Surface area measurements were then conducted using nitrogen as the adsorbate. These measurements will be described in detail in Section III. At the completion of these measurements the evacuated bulb was again immersed in liquid oxygen.

The sample was equilibrated with oxygen at -183°C. by admitting a known volume of oxygen into the bulb. The liquid oxygen was removed and the bulb allowed to return to room temperature in the presence of a finite pressure of oxygen. The equilibrium pressure was recorded and then oxygen in the gas phase was pumped away. From the known volumes of the apparatus, together with the decrease in pressure, the volume of oxygen adsorbed by the nickel was calculated.

The furnace was placed in position and the temperature of the samplemaintained at 300°C. Tap T_3 was shut thus isolating the evacuated bulb and the burette system

was filled with oxygen at about 5 cm.Hg. pressure. The mercury level in the manometer was adjusted such that the light (L) was flicking on and off due to the vibration of the mercury surface in contact with the platinum wire. Tap T_1 was opened and the time noted. The pressure in the system fell, but this was counteracted by raising the mercury level in the burette. The level was raised until the light was just extinguished. The time when the lamp again became illuminated, together with the burette reading, was noted. The level in the burette was then raised by another notch on the winch and the procedure repeated.

In later experiments the furnace was replaced by a vapour bath similar to that shown in fig.(1b) and kinetic measurements were undertaken at 180°C., the boiling point of aniline.

RESULTS :

The results have been divided into two groups:-

(a) Kinetic Results,

(b) Modified Apparatus Results.

Kinetic Results

Table (4) lists data relevant to some twenty kinetic runs. The results are plotted in fig.(10) and fig.(11).

Modified Apparatus Results

These results have been further subdivided into two groups :-

TABLE (4)

Run	Wt. of Ni (Gms.)	Time and Temp. of Dehydrat.	Time and Temp. of Decomp.	Vol. O_2 Abs. at -183 and 20°C. (Cms.³ S.T.P./Gm.Ni)	Total Vol. O_2 at -183 and 20°C. +Vol. after 60 min. Oxid. at 300°C. (Cms.³ S.T.P./Gm.)	% Oxidation	Remarks
4.	0.017	2 h. at 204°C.	2 h. at 330°C.	39.7	105.6	55.3	Red glow at 20°C.
5.	0.022	"	"	-	66	34.9	" " " "
6.	0.017	"	"	85.6	138	72.3	O_2 admitted at -183°C. No red glow at 20°C.
7.	0.027	"	"	76.8	146	76.5	No red glow.
8.	0.019	"	"	7.4	101	52.9	Ground glass glass wool. No glow.
9.	0.017	"	"	Negligible	98	51.4	" " " "
10.	0.021	"	"	39.[illegible]	114	59.7	" " " "
11.	0.019	"	"	30.6	108	56.5	" " " "
12.	0.019	"	"	13.4	110	57.6	" " " "
13.	0.019	"	"	6.5	89	46.6	" " " "
14.	0.014	"	"	73.3	150	78.6	Ground Glass absent. Glass Wool present.
15.	0.018	"	"	124.3	150	78.6	" " "
17.	0.018	"	"	68.8	150	78.6	Ground Glass, Glass Wool absent.

18.	0.0089	"	"	68.3	150	78.6	Ground Glass, Glass wool absent.
20.	0.0 3	"	"	Negligible	118	61.8	" " "
21.	0.0099	"	"	Negligible	96	50.3	" " "
22.	0.021	"	"	46.2	140	73.4	" " "
23.	0.015	"	"	Negligible	130	68.1	" " "
24.	0.016	"	"	Negligible	94	49.2	" " "

...

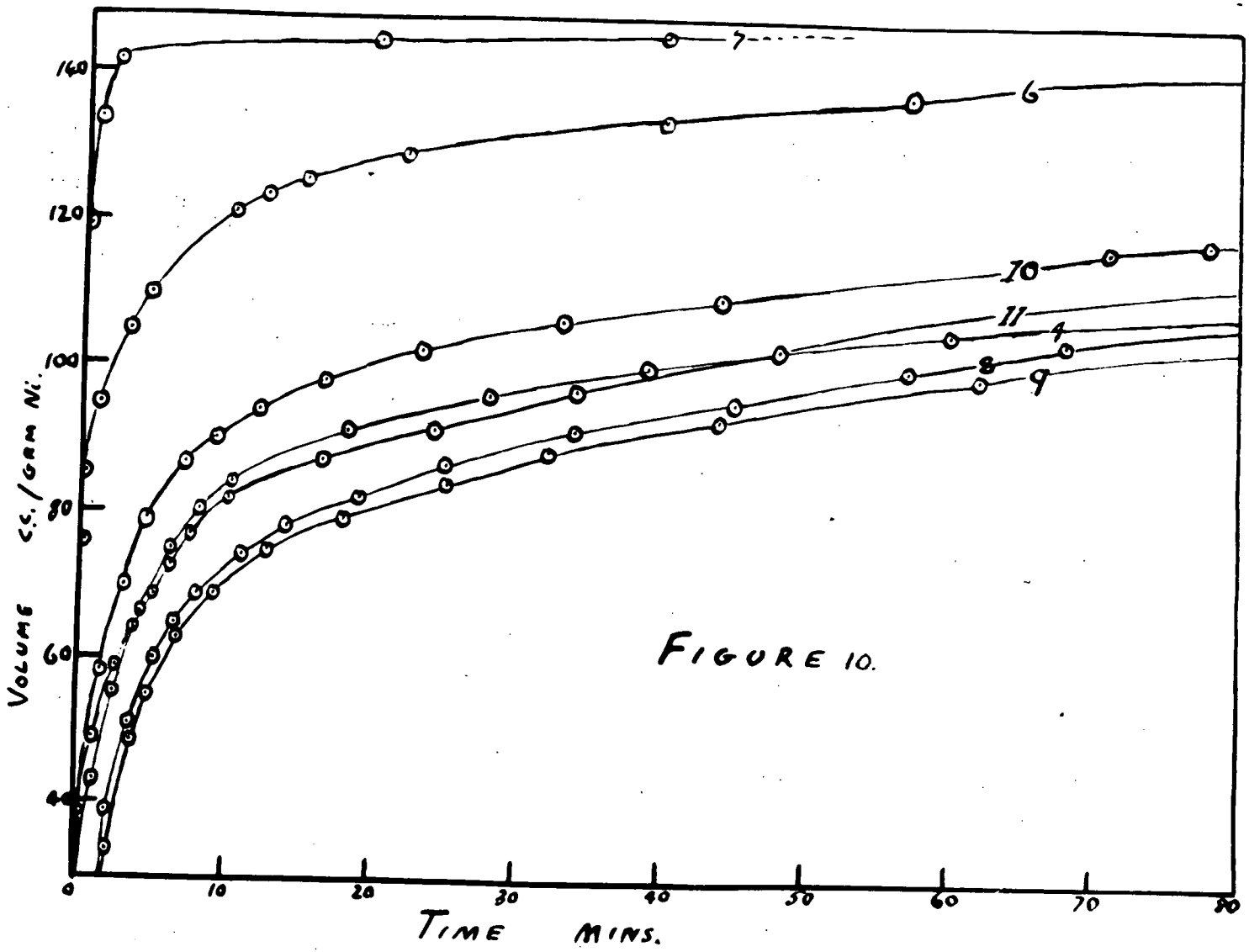

7
6
10
11
4
8
9
140
120
100
80
60
40
VOLUME cc./GRM Ni.
0
10
20
30
40
50
60
70
80
TIME MINS.

FIGURE 10.

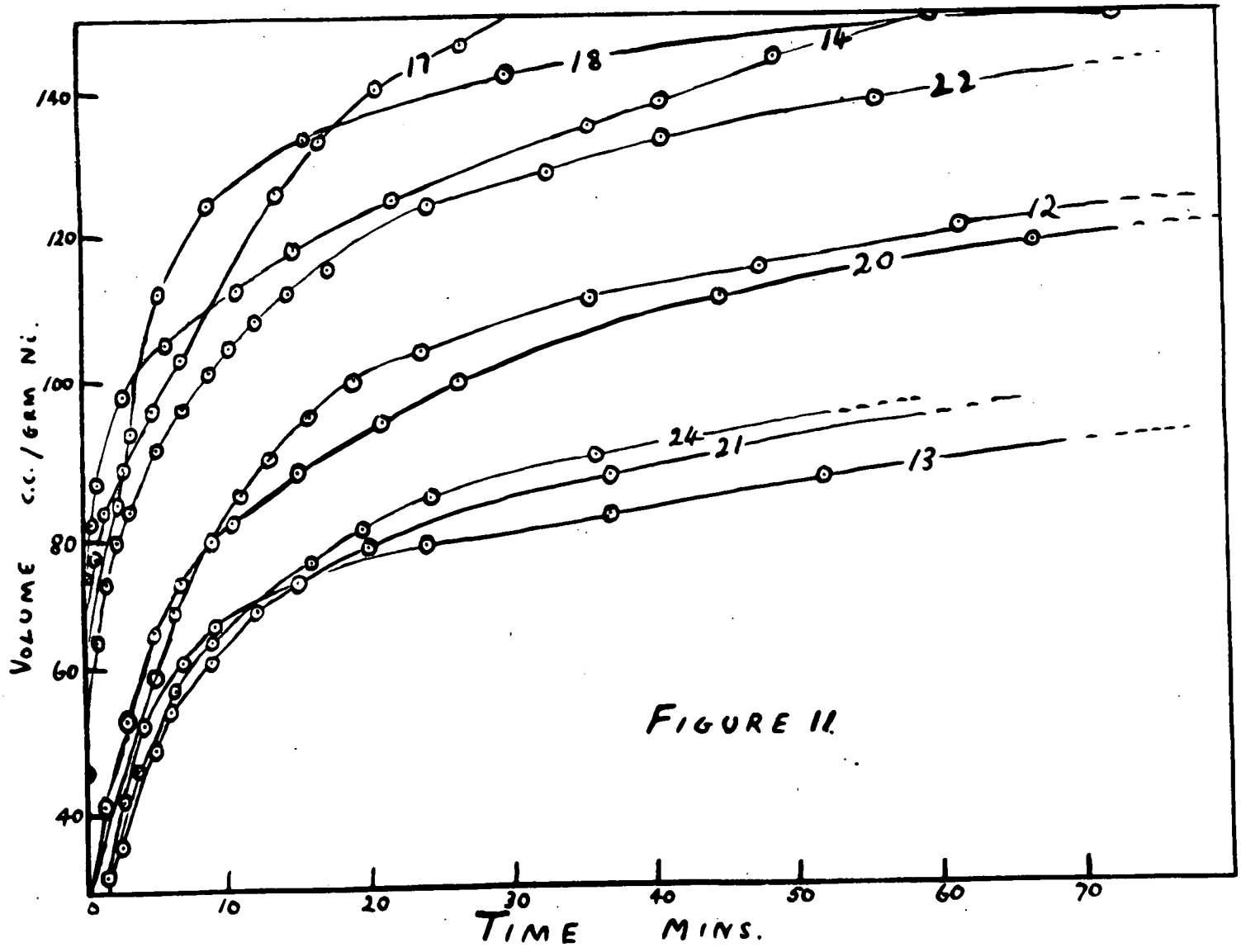

17
18
14
22
12
20
24
21
13
140
120
100
80
60
40
0
10
20
30
40
50
60
70
VOLUME c.c. / GRM Ni.
TIME MINS.

FIGURE 11.

(1) Surface Area Results,

(2) Oxidation Results.

(1) Surface Area Results

Details of the surface area measurements are given in Section III but some relevant results will be mentioned here.

(i) The thermal decomposition of nickel oxalate at 330°C. yielded nickel powders the surface areas of which varied in the range 22 - 11 m^2/gm.Ni.

(ii) An increase in the time of decomposition at constant temperature resulted in a decrease in surface area.

(iii) An increase in the temperature of decomposition reduced the surface area.

(iv) Identical runs as far asweight of nickel oxalate, time and temperature of dehydration and decomposition failed to yield identical surface areas.

(v) After sintering the nickel powders at 500°C. for six hours the surface area was reduced to 2m^2/gm.Ni, a figure which was reproducible from run to run.

(2) Oxidation Results

Accurate kinetic measurements were not obtained with the modified apparatus because the reaction was too fast at 300°C. The temperature of oxidation was reduced to 180°C., but the rate was still excessive. The volumes of oxygen used,

together with other data, including some surface area results, are given in Table (5).

DISCUSSION

The discussion of the results has been subdivided under the following headings:-

(a) Modifications made to improve the Reproducibility,

(b) Surface Area Results,

(c) Pyrophoric Character of the Powders.

(a) Modifications made to improve the Reproducibility

A glance at Table (4) and fig. (10) and fig.(11) indicates immediately the inconsistency of the results. Various steps were taken from run to run to standardize or eliminate factors thought to be effecting the rate of oxidations. These steps have been summarised under the heading "Remarks" in Table (4) but will be discussed in greater detail.

(i) Preliminary Saturation with Oxygen

Admission of oxygen at room temperature to the fresh nickel powder produced a bright red glow in the material. This vigorous oxidation varied in extent and intensity from run to run. In an effort to standardize this irregularity the nickel was saturated with oxygen at $-183^{\circ}C$. and then brought to room temperature under a finite pressure of oxygen. This treatment apparently masked the pyrophoric character

TABLE (5)

Run No.	Time and Temp. of Dehyd.	Time and Temp. of Decomp.	Time and Temp. of Sinter.	Wt. $NiC_2O_4 . 2H_2O$	Wt. Ni	S.A. Ni Before Sinter.	S.A. Ni After Sinter.	Vol. O_2 at 20°C. per Gm.Ni	% Oxid. at 20°C.	S.A. Ni after 20°C. Oxid.	Vol. O_2 180°C. per Gm.Ni	% Oxid. at 180°C.	Tot. O_2 per Gm.Ni	% Oxid.	S.A. Oxid. Ni	Remarks
1.	24 h. at 202°C.	24 h. at 330°C.	-	1.085	0.348	-	-	39.49	20.7	-	112.5	58.9	154.2	80.8	-	
2.	21 h. at 203°C.	16¼ h. at 312°C.	-	3.906	1.254	20.7	-	16.33	8.66	19.63	43.3	22.69	59.63	31.24	19.7	
3.	21 h. at 203°C.	16 h. at 323°C.	-	4.056	1.303	19.7	-	21.17	11.09	17.28	82.63		103.8	54.4	13.2	
4.	22 h. at 196°C.	16 h.at 286°C. 24 h.at 330°C.		4.115	1.321	15.3	-	6.53	3.42	15.83	27.39	14.35	33.91	17.77	16.7	
6.	22 h. at 216°C.	24 h. at 330°C.	6 h.at 500°C.	4.299	1.380	15.0	2.0	2.99	1.56	2	14.44	7.57	17.43	9.13	-	
7.	24 h. at 210°C.	30 h. at 330°C.	6 h.at 500°C.	4.50	1.445	-	2.1	2.89	1.52	-	14.09	7.38	16.99	8.90	-	
8.	24 h. at 212°C.	12 h. at 345°C.	3 h.at 500°C.	4.28	1.37	-	2.0	3.42	1.79	-	32.77	17.17	36.19	18.96	-	
9.	23 h. at 208°C.	23 h. at 346°C.	6 h.at 505°C.	1.136	0.37	-	-	5.45	2.86	-	78.4	41.09	83.9	43.9	-	Burette B_1 off O_2 admitted in two lots. 1 min. between admissions.
10.	8 h. at 210°C.	24 h. at 345°C.	6 h.at 505°C.	1.15	0.374	-	-	3.34	1.75	-	55.6	29.15	58.99	30.91	-	B_1 off. O_2 admitted in two lots. 30 min. between.
11.	21 h. at 220°C.	24 h. at 352°C.	6 h.at 503°C.	1.165	0.374	-	-	4.07	2.13	-	107.68	56.42	111.75	58.56	-	B_1 and B_2 opened together. Thermo-couple rise 150°C.
12.	24 h. at 220°C.	24 h. at 334°C.	6 h.at 505°C.	1.137	0.365	-	-	3.48	1.83	-	89.11	46.68	92.6	48.5	-	B_1 admitted Thermo-couple rise 100°C. B_2 admitted after 10 min. No temp. change.

because no red glow was observed when a fresh supply of oxygen at 20°C. was admitted to the evacuated, presaturated sample. This procedure was adopted in all runs.

(ii) Factors Associated with Packing

Examination of the powders after oxidation showed the top portion greyish in colour, while the bottom was usually black. This suggested that only the top portion was being extensively oxidized. This is supported by the fact that the percentage oxidation was never greater than 80 and usually much less than this. It was decided to disperse the powder thus allowing easier access for the oxygen. Three methods were tried.

(a) Mixing with ground glass:-

An equal volume of ground glass was mixed with the nickel oxalate dihydrate prior to decomposition.

(b) Two plugs of glass wool:-

When only one plug of glass wool was used in the ampoule, the nickel powder adhering to the wool was finely dispersed and judging by the change in colour was completely oxidized. The amount adhering was variable from run to run. In an effort to standardize this factor the sample, mixed with ground glass, was wedged in between two glass wool plugs.

No improvement in consistency was obtained with either modification so the use of both ground glass and glass wool was abandoned after a few runs.

(c) Larger ampoule:-

The size of the ampoule was increased by a factor of three and the powder was spread out in a thin layer on the floor of the ampoule. Although the dispersion of the powder was good no increase in reproducibility was evident.

(b) Surface Area Results

It had been assumed that the thermal decomposition of nickel oxalate under identical conditions would yield nickel powders possessing the same properties. However, because efforts to improve the consistency of the runs had been futile it was necessary to check whether such an assumption was justified. Thus, the apparatus was modified and the surface areas determined.

Although the surface areas could not be reproduced exactly from run to run it is doubtful if the variation is sufficient to account for the poor kinetic results. In the case of the sintered samples, although no significant kinetic results were obtained the variation in the percentage oxidation (Table (5)) would suggest that kinetic plots would be variable.

It may be seen from Table (5) that the volumes of oxygen consumed per gramme of sintered nickel at -183° and 20° C. are approximately of the same order of magnitude. This may be contrasted with the results shown in Table (4), where the samples were not sintered. This improvement in consistency may be

due in part to the elimination of the surface area variable in the sintered samples.

(c) Pyrophoric Character of the Powders

Two important facts may be seen from the results shown in Table (5) especially runs 9 - 12.

(i) The extent of oxidation was a function of the volume of oxygen which could be admitted in the first instant.

(ii) If two burettes containing oxygen were opened to the sample together, then a greater volume was adsorbed than if the second burette was opened one minute after the first.

These results suggested that the presaturation of the nickel at -183 and 20°C. did not eliminate the vigorous oxidation due to the pyrophoric nature of the powders. In order to test this suggestion a crude calorimeter was built to measure the temperature rise of the sample when oxygen was admitted at 300°C. A copper constantan thermocouple, made from fine wire, was cemented to the bottom face of the adsorption bulb. When a large volume of oxygen was admitted at 300°C. to the presaturated sample the thermocouple indicated a rise in temperature of 150°C. The temperature rise was proportional to the volume of oxygen admitted in the first instant. Because of the poor thermal contact, the temperature rise in the sample was probably much greater than indicated by the thermocouple.

These few experiments clearly indicate that although presaturation at - 183° and 20°C. did reduce the effect due to the pyrophoric nature of the powders it did not eliminate this factor. Further more, the elimination or control of the other factors thought to influence the rate of oxidation did not enhance the consistency of the results. These facts suggested that the pyrophoric nature of the powders played a dominating role in influencing the rate of oxidation.

In view of this evidence, there is little need to comment on the kinetic plots given in fig. (10) and fig. (11). Presumably in the case of runs 7 and 17, where a fast reaction occured, the oxygen was readily available to the majority of the sample and the temperature rise was probably considerable. In the other runs where slower rates and somewhat similar plots were obtained the controlling factor was probably the passage of oxygen into the mass of the powder.

As no method of eliminating or controlling this pyrophoric factor was evident it was decided to terminate the kinetic studies.

SECTION III.

SECTION III

INTRODUCTION:

As indicated in Section II at a stage in the oxidation investigation it was decided to measure the surface areas of the nickel powders. These powders were produced in situ by the thermal decomposition of nickel oxalate. It was desirable that the surface area measurements would not contaminate the powders rendering them unsuitable for subsequent oxidation. The obvious method was gas adsorption at low temperatures. Before describing the experimental procedure a discussion of the various isotherms will be given. The literature devoted to this subject is, however, so vast that a detailed review will not be attempted. Instead an examination of some of the more important papers will be made, with a view to assessing the relative merits of the several isotherms.

Literature Survey:

At the time of writing there are four generally accepted accurate methods for the determination of the areas of finely divided solids by gas adsorption. They are:-

1. The absolute method of Harkins and Jura which is based on sound thermodynamics (61).

2. The method of Brunauer, Emmett and Teller (B.E.T.) based on kinetics (62).

3. The Huttig method based on kinetics (63).

4. The relative method of Harkins and Jura based on the characteristics of condensed films (64).

Of these methods the absolute method of Harkins and Jura is perhaps the most accurate and has a sound theoretical basis. However, it is experimentally the most difficult and cannot be used with porous or coarse powders. Its usefulness lies in the fact that it can be and is used to standardize the other methods. For example, the B.E.T. and Huttig methods themselves cannot give the area of any solid whatever, since from the adsorption isotherm only the number N of molecules in what is supposed to be a complete monolayer can be obtained. The area of any solid is given by -

$$\Sigma = N\sigma$$

where σ the mean area occupied per molecule in the complete monolayer is unknown.

Emmett and Brunauer (65) have given a geometrical method for calculating the value of σ. They assume that the molecules are spherical and that the packing in the monomolecular film is the same as the molecules of the solidified gas in their plane of closest packing. The equation which they use is -

$$\sigma = 4\,(6.866)\left(\frac{M}{4\sqrt{2}\,N_A\,\delta_S}\right)^{2/3}$$

where M = the molecular weight

N_A = Avagadro's Number

δ_S = density of the solidified gas.

In certain cases δ_s is replaced by δ_L the density of the liquidified gas where evidence tends to support the idea that the film is liquid condensed and not solid condensed.

Hill (66) gives an alternative method of calculating σ based on Van der Waal's equation. For several gases the latter method gives values in fair agreement with the more usually accepted Brunauer Emmett values.

Harkins and Jura on the other hand prefer to calculate the value of σ by comparing the B.E.T. surface areas with those measured by their absolute method. They have calculated the "correct" surface area of a sample of anatase using their absolute method. Adsorption isotherms of several different vapours were then determined and the surface areas calculated by the B.E.T. method. The σ values necessary to give agreement with the "correct" surface area were calculated and compared with the values obtained by the geometrical method of Brunauer and Emmett. They conclude that the Brunauer Emmett values become more greatly in error as the vapour molecule becomes larger. In the case of nitrogen the gas most commonly used in surface area measurements, the σ value are the same by either method.

Pickering and Eckstrom (57) have measured the physical adsorption of N_2, Kr, A, CO and CO_2 on a sample of anatase having a surface area of 13.0 m^2/gm. as determined by

the absolute method. From the results they calculated σ values which are in poor agreement with liquid density measurements in contrast to the results of Harkins and Jura.

Livingston (68) has measured the adsorption isotherms of nitrogen, water, propane and heptane on four finely divided solids. He calculated σ values for water, propane and heptane to give agreement with the nitrogen surface area. However, in order to obtain values which were in agreement with values determined by density, X ray and film balance techniques it was necessary to choose a value of 15.2 Å^2 instead of 16.2 Å^2 (the value usually accepted) for the mean area occupied per nitrogen molecule.

The uncertainty in accepting the Brunauer Emmett method of calculating σ values is further emphasized by the results of Beebe, Beckwith and Honig (69). In a paper in which they introduce the use of krypton adsorption for surface areameasurements on materials of low adsorbive capacity, Beebe et al find it necessary to assume a value for the mean area per molecule of krypton greatly in excess of that calculated by the Brunauer Emmett method, in order to obtain agreement with the results obtained by the Harkins Jura absolute method. This result is supported by later work of Davis and Dewitt (70).

THE BRUNAUER EMMETT TELLER (B.E.T.) ISOTHERM

The B.E.T. theory of physical adsorption was the first and is still probably the best and most useful theory of multimolecular adsorption, covering the complete range of pressure. This is not to say, however, that it is really a satisfactory theory. The assumptions upon which it is based are wrong in some cases and crude in others but they are still sufficiently good to contain a number of important qualitative features actually observed experimentally.

Brunauer Emmett and Teller gave a kinetic derivation (62) of the B.E.T. equation which is really a generalization of Langmuir's kintetic derivation of the Langmuir isotherm (71). The derivation involves a balancing of the evaporation and condensation phenomena in adjacent layers with the assumption that only the energy of adsorption of the first layer differs from the energy of condensation. The final equation is -

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \cdot \frac{P}{P_o}$$

in which V is the amount of gas adsorbed at the equilibrium pressure P, P_o is the saturation pressure and V_m the quantity of gas required to form a monolayer. C is a constant which is a function of the difference between the energy of adsorption in the first layer and the energy of condensation. A plot of $\frac{P}{V(P_o - P)}$ against $\frac{P}{P_o}$ should give a straight line

from the intercept and slope of which the constants V_m and C can be calculated. If the average area σ occupied per molecule in the monolayer is known the specific area of the solid may be calculated.

Cassie (72) and Hill (73) have provided a statistical deduction of the B.E.T. equation. The usefulness of a statistical mechanical treatment lies in its explicit provision of all constants, parameters etc. in terms of molecular properties. In addition the question of particular kinetic mechanisms can be avoided, it being necessary to consider only the various possible accessible states of the system.

Theoretical Considerations

The B.E.T. theory has been severely criticised because of the several unsound assumptions upon which it has been based. Harkins (74) lists five unsound assumptions.

1. The lateral interaction between molecules in the first layer can be neglected.

2. Inhomogeneities of the surface of the solid have a negligible effect.

3. The energy of interaction of the second layer with the material underneath it does not differ from that of the n^{th} layer with the n -1 layer where n is large.

4. The surface energy of the film can be neglected.

5. The energy of adsorption in a layer is independent of the amount already adsorbed in that layer.

Harkins has also pointed out that it is possible to describe the solubility of ammonia in water at 20°C. by a B.E.T. equation. A fit of experimental data to a B.E.T. equation is not evidence that the phenomena under discussion is even one of adsorption.

Hill (75) has attempted to compensate for the neglect in the theory of the horizontal interaction especially in the first layer, but has met with only limited success.

Halsey (76) has discussed the imperfections of the B.E.T. theory to some length. He concludes, however, that refinements to the actual theory appear to destroy rather than enhance the ability of the B.E.T. equation to fit isotherm data.

Smith and Pearce (77) have suggested that the whole basic model of the B.E.T. theory is incorrect. They believe that instead of being essentially of uniform activity, the surface of a solid is composed of regions of varying activity. This approach gains support from calorimetry studies on heats of adsorption.

Pierce, Wiley and Smith (78) support the idea that

capillary condensation plays a much larger role in adsorption at low relative pressures than is generally accepted. They base this conclusion on adsorption measurements of several vapours on charcoal. If this is so then the V_m values are incorrect and the surface area values as generally given are much too large.

Practical Considerations

Despite the theoretical limitations the B.E.T. equation has achieved considerable practical success in recent years. Nevertheless a number of modifications to the basic B.E.T. equation have been suggested. In all cases, however, they are designed to extend the range over which the equation will fit experimental data. The original B.E.T. equation is only operative in the range $0.05 < \frac{P}{P_o} < 0.35$. Outside this range the neglect of various factors in its derivation appear to render the B.E.T. equation invalid. Anderson (79) has modified the B.E.T. equation by mutiplying the relative pressure P/P_o by a factor less than one. When this factor lies between 0.6 - 0.7 the equation is found to give a straight line up to a relative pressure of 0.7. The constant, although impirical, has been interpreted to mean that the free energy of adsorption in the second to tenth layers is less than the free energy of liquefaction.

Picket (80) has also suggested modifications to the B.E.T. equation in order to extend the range of fit of

experimental data. The modification necessary is found by trial and error and once found does not alter the values of V_m or C, but simply extends the number of points through which the straight line may be drawn.

Cooke and Dole (81) amongst others have made semi-impirical modifications which have led to an improvement in agreement with experimental data. Provided a straight line is obtained for a portion of the isotherm ($0.05 < P/P_o < 0.35$) the B.E.T. equations either as such, or modified, gives values for V_m which are reproducible and self-consistent with different gases. If a reasonable value of σ is used the surface areas calculated from the V_m results are in good agreement with other methods.

THE HUTTIG EQUATION

Huttig (63) has derived an adsorption isotherm -

$$\frac{P}{V} \cdot \left(1 + \frac{P}{P_o}\right) = \frac{P_o}{V_m C} + \frac{P}{V_m}$$

where C is the B.E.T. constant, by a fundamental modification of the B.E.T. argument (62). Huttig assumes that the rate at which the number of molecules in the second layer increases is proportional to the number of uncovered first layer molecules (in agreement with the B.E.T. derivation) and the rate at which this number decreases is proportional to the total number of molecules in the second layer (in disagreement with the B.E.T. theory which uses instead the number of uncovered second layer molecules). Other-wise the assumptions of the two theories are identical.

Ross (82) has examined the theory in some detail and Fergusson and Barrer (83) have given a statistical mechanical derivation. Hill (84) has criticised the equation on theoretical grounds and has also pointed out the fallacy in the statistical argument of Fergusson and Barrer. The numerous criticisms of the B.E.T. theory can equally well be applied to the Huttig isotherm.

From the practical point of view the Huttig equation is successful. Ross (82) has shown that the Huttig equation will give a linear graph up to a relative pressure of 0.85, which may be compared with the B.E.T. upper limit of 0.35. This means that more points are available and hence a line can be fitted with greater ease and accuracy. The B.E.T. and Huttig equations yield V_m values which are approximately equal for a given set of isotherm data (85).

Corrin (86) has compared the B.E.T. and Huttig equations for the case of nitrogen and argon at -195°C. on several carbon blacks. The author concludes that the B.E.T. equation is superior to the Huttig giving more self consistent results for different gases on the same adsorbents.

Schreiner and Kemball (87) have found, on the whole, good agreement between the Huttig and B.E.T. surface areas of several metallic oxides using different adsorbates.

Barrer, McKenzie and McLeod (88) have compared the

B.E.T. and Huttig surface areas using a value for the mean area per molecule of nitrogen derived from the Harkins Jura absolute method. In addition these workers have developed a series of B.E.T. type multilayer isotherms which have also been tested. Agreement between all methods is only fair, a result which raises the question of absolute as against comparative accuracy of surface area measurements through adsorption. The authors conclude that it is not enough to determine the surface area always by a single type isotherm, but rather to employ a group of isotherms to check the areas obtained with each against those obtained with the others. This could give a better idea of the probable absolute accuracy of such determinations.

THE RELATIVE METHOD OF HARKINS AND JURA

This method is similar to both the Huttig and B.E.T. methods in that it must be standardized by the absolute Harkins Jura method. Its success depends on the properties of condensed films. A film is said to be condensed whenever it exhibits a linear relation between surface pressure π and the mean area σ occupied per molecule,

i.e. $\pi = b - a\sigma$ where a and b are constants.

This may be transformed with sufficient accuracy into -

$$\log. P/P_o = B - \frac{A}{V^2}.$$

If, therefore, log. P/P_o is plotted against $\frac{1}{V^2}$ a linear graph is obtained when the film is condensed. It was shown by Harkins and Jura (64) that as the area of the solid increased

the numerical value of A also increased. They were able to show that the surface area Σ was related to A by the equation -

$$\Sigma = k A^{\frac{1}{2}}.$$

The value of A is computed from the linear plot of log. $P/P_0 \sim \frac{1}{V^2}$ and k is calculated. Harkins and Jura have calculated a value of k for four adsorbates, but these have been extended by other investigators. With different adsorbates or different temperatures the value of k is different.

The major difficulty in the Harkins Jura relative method lies in evaluating the constant k. The Harkins Jura absolute method has been confined to a sample of anatase and the "correct" surface area computed. A value of k to give the same area by the relative method is chosen and the assumption is made that K is constant and independent of the adsorbent. In a number of cases with different adsorbents it was found necessary to alter the value of σ with k constant to obtain surface areas which would agree with B.E.T. and Huttig values, these latter methods having previously been standardized against the absolute method. This aspect has been investigated at length by Corrin (89). He concludes that the value of the constant k is not always the same, especially in those cases where the plot log $P \sim \frac{1}{V^2}$ gives two or more linear portions of different slopes. Under these circumstances it is necessary to take the ratio of the square root of the slopes of the different

linear portions to decide which value of k to use. When only one straight line is obtained it is impossible to decide which value to take. To overcome this it is necessary to calculate the surface area by either the absolute method or the B.E.T. or Huttig equations and choose the appropriate value of k to give agreement.

Harkins and Jura (90) have considered in detail the manner in which the area occupied by a molecule of nitrogen varies for different adsorbents. In this treatment they have assumed that k has always the value obtained from the absolute method on the anatase sample. For over ninety different adsorbents the constants for the Harkins Jura relative and B.E.T. equations were determined. The specific surface Σ was calculated from the equation -

$$A = \Sigma^2 / k^2$$

using a constant value of k, and σ was calculated from the equation -

$$\Sigma = N V_m \sigma / V$$

where N is Avagodro's number and V the volume occupied per mole.

As Emmett (91) and Livingston (92) have pointed out there is no need to assume k constant and σ variable. It seems plausible that k may vary from substance to substance and yet σ remain constant. This latter alternative, however, does not gain support from the fact that frequently it is necessary to assume different values of σ for the same gas on different

adsorbents in order to obtain agreement between B.E.T. computed surface areas.

Joyner and Emmett (93) have compared the B.E.T. and Harkins Jura relative methods for nitrogen on several carbon blacks at - 205, -195 and -183°C. respectively. They have used the Harkins Jura value of k at -195 and from the results calculated the correct value of k to give consistent areas at the other temperatures. The variation of k with temperature is in approximate agreement with the prediction of Davis and Dewitt (94), that for a given adsorbate the constant k should be proportional to $\frac{1}{T^{\frac{1}{2}}}$.

Joyner and Emmett (95) have carried out similar calculations for k on porous glass but do not obtain agreement between the k values at -205° on porous and non-porous materials. This suggests that the temperature coefficient of k may be different for porous and non-porous substances.

Comparision of the B.E.T. and Relative Methods

Despite the uncertainty in the choice of constants the agreement between the surface areas calculated by the Harkins Jura Relative and the B.E.T. methods is good (93) (94), (95), (96). As Livingston (97) points out, however, this is to be expected since when the B.E.T. constant C. is in the range 25 - 250 the two equations both give satisfactory fits to the same adsorption data (98), (99), (92) and Harkins

and Jura (64) have chosen their k values to be consistent with the B.E.T. adsorption results obtained with anatase.

Agreement, however, is not always observed. Porous adsorbents that form multi layers only a few molecules thick do not give adsorption data that agree with the standard B.E.T. equation. However, they do agree with the B.E.T. "n" equation which is similar to the ordinary B.E.T. equation but contains exponential n terms in which n equals the maximum number of molecules in the monolayer at $P = P_0$. Joyner, Wienberger and Montgomery (100) found that when n was small the Harkins Jura method could not be used. Smith and Bell (101) have shown that this result would have been predicted from a mathematical treatment of the "n" equation.

The relative merits of the methods which have been discussed appears to depend largely on the significance placed on the surface area values. It is doubtful if any of the methods will give the absolute surface area. This is unlikely because of the following points:-

1. The uncertainty in allotting a value for σ at a definite temperature for a particular adsorbate.

2. The unknown influence of capillary condensation and active centres on the formation of a monomolecular film with a subsequent uncertainty in the value of V_m.

3. The unsound assumptions upon which the B.E.T. theory

is based and the fact that the theory deviates more widely from experimental data when refinements to the basic assumptions are incorporated in the final equation. Similar arguments apply in the case of the Huttig equation because the basic assumptions are identical to those in the B.E.T. equation with one exception.

In the case of the Harkins Jura relative method the uncertainty involved in the value of k renders the complete acceptance of surface areas by this method open to doubt.

Only in the case of the Harkins Jura absolute method can complete reliance be placed in the values obtained. Unfortunately the experimental difficulties are such that only a few measurements on a single sample of anatase have been completed. As indicated, both the Harkins Jura constant k and the value of σ used in the B.E.T. equation have been selected to give agreement with the absolute result.

This agreement has not always been found with some other adsorbents. In the first place Harkins Jura absolute results are lacking and secondly the B.E.T. and Harkins Jura relative results vary from one adsorbate to another for a given adsorbent. This variation has been attributed to a change in the values of k and σ either singly or together, but it may in fact be due to capillary condensation,

active centres or some other complicating factor. It is desirable that the absolute measurements be extended to other adsorbents and the results compared with the B.E.T., Huttig and Harkins Jura relative values. By this means it would be possible to determine whether or not the values of σ and k are in fact different for various adsorbents.

In the absence of such comparisons one is drawn to the conclusion that complete acceptance of surface area values by any one method is unwise. For comparative studies, especially with adsorbents of identical or similar chemical composition, the values obtained by the three methods taken together should indicate differences or changes in surface area.

Adsorbates

Little mention has been made of the type of adsorbate used in surface area measurements. The most convenient are nitrogen, argon, krypton and carbon monoxide at -195° or -183°C. Other vapours, including carbon dioxide, water, propane, butane, ethylene, etc., have been used at various temperatures but generally speaking these vapours require a more complicated adsorption apparatus.

Beeck (102) has criticized the use of nitrogen as an adsorbate following heat of adsorption measurements on evaporated metal films. He showed that some chemisorption of nitrogen took place and therefore V_m values as usually

determined would be in error. Such criticism has not been substantiated in surface area results, suggesting that the effect is of minor significance in most cases. Nevertheless, the adsorption of krypton and argon appears now to be more generally favoured.

Brunauer and Emmett (103) have indicated that it is possible to obtain agreement in surface area measurements despite chemisorption. They have investigated the case of carbon monoxide adsorption on an iron ammonia catalyst and provided the volume of chemisorbed gas is subtracted from the total volume of gas adsorbed, then satisfactory agreement is obtained with surface area results using gases in which chemisorption is absent.

In the present investigation on nickel powders it was decided to include measurements with gases where chemisorption was absent, slight and appreciable. The apparatus was designed for nitrogen adsorption but was equally suitable for the adsorption of argon and carbon monoxide at -183°C. It was hoped that the results could be plotted according to the various isotherms thus allowing a comparison of the methods to be made.

EXPERIMENTAL:

(a) Reagents

1. Nickel Powders:-

These powders were prepared by the thermal decomposition of nickel oxalate. Details of the preparation are given in Section II.

2. Nitrogen:-

In the initial surface area measurements "pure" cylinder nitrogen containing about 1% oxygen was purified by passing through pyrogallol and over hot freshly reduced copper gauge. This system was satisfactory for preliminary measurements during the oxidation studies, but was inconvenient and subject to leakage. It was decided therefore to incorporate an all glass purification train in the apparatus. It was similar to that used by Herington and Martin (104) and is shown diagramatically in fig.(12) and in the photograph fig. (13).

It consisted of four adsorption towers, each about 40 cms. in height and 30 mm. in diameter. The first two contained a 1:1 solution of concentrated ammonia (d = 0.88) and saturated ammonium carbonate solution with a bed of tightly packed fine copper gauze, separated from the lower part of the tower containing the solution by glass rods. These first two towers were to absorb oxygen. The next two towers contained packed beds of Raschig rings with

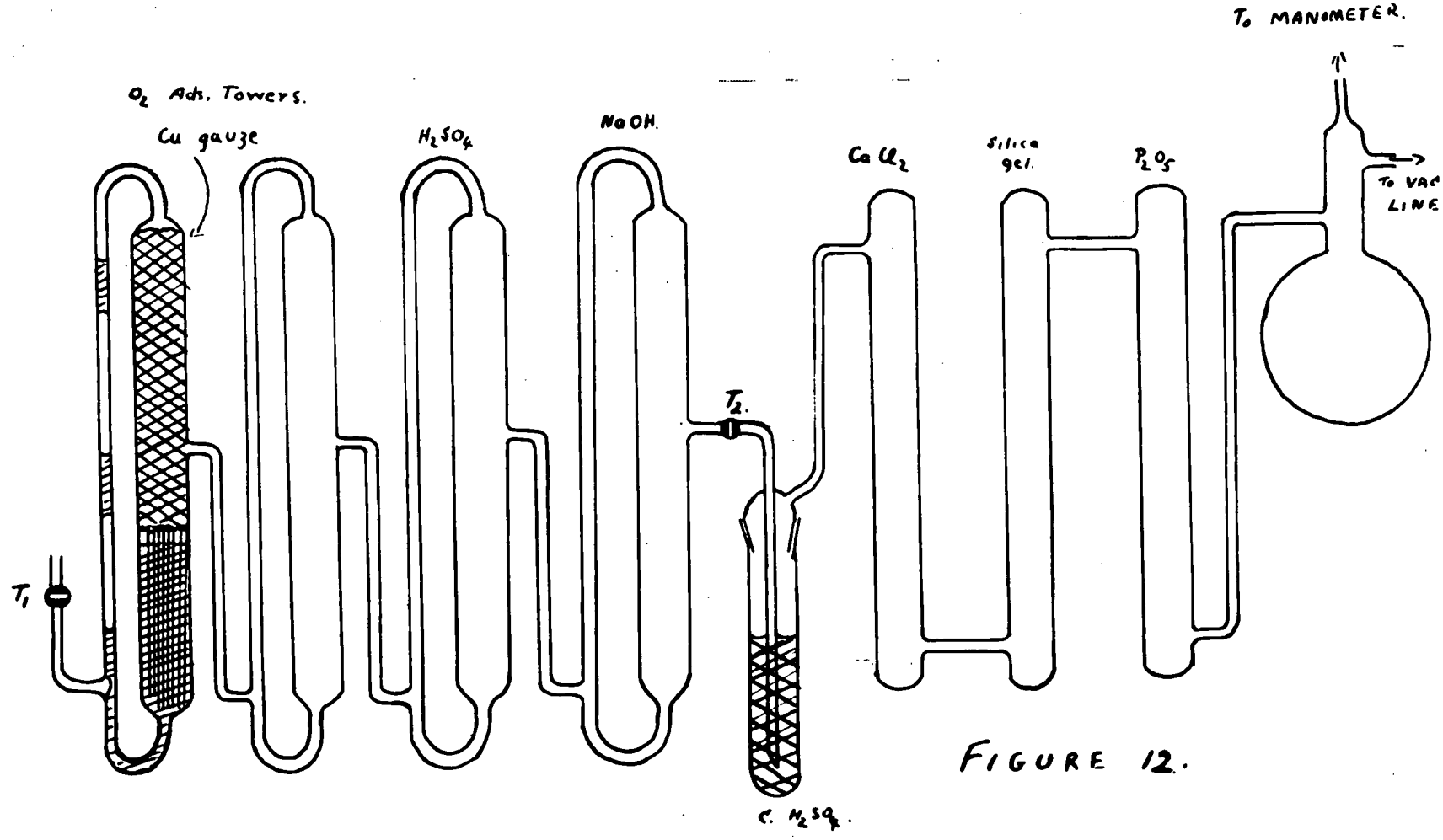

T_0 MANOMETER.
O_2 Ads. Towers.
Cu gauze
H_2SO_4
NaOH
$CaCl_2$
silica gel.
P_2O_5
To VAC LINE
T_1
T_2.
C. H_2SO_4.

FIGURE 12.

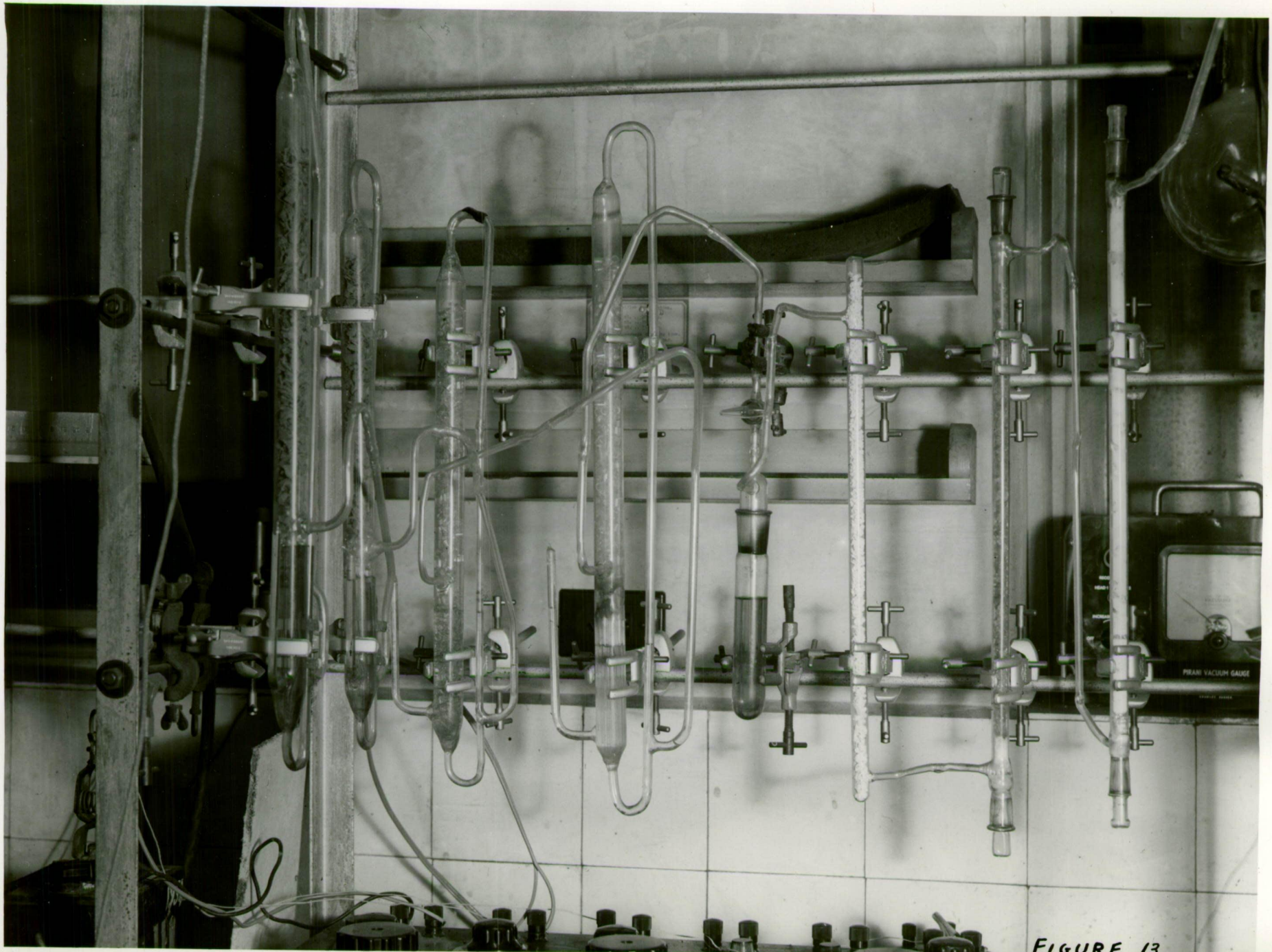


FIGURE 13.

a solution of 25% H_2SO_4 to adsorb ammonia in the third tower and a 10% solution of NaOH to absorb carbon dioxide in the last tower. The gas leaving the towers was then bubbled through concentrated sulphuric acid and then through drying tubes containing calcium chloride, silica gel and lastly phosphorus pentoxide. The nitrogen was stored in a litre reservoir, the pressure being recorded by a mercury manometer of the atmospheric "blow off" type. The system worked extremely well and was easy to operate. Tap T_2 was used to isolate the drying agents from the wet towers when the system was not in use.

3. Carbon Monoxide:-

Carbon monoxide was prepared by dropping air free formic acid on to concentrated sulphuric acid at 120 - 150°C. The purification train is shown in fig.(14). Flask A contains concentrated sulphuric acid heated by a glycerol bath not shown. B is a dropping funnel containing formic acid, freed from much of its dissolved air by shaking in a flask which was continuously evacuated. D and E are scrubbing towers filled with 50% KOH and a mixture of one part 30% pyrogallol and two parts 50% KOH. F and G are drying towers containing $CaCl_2$ and P_2O_5 respectively. H is a liquid air trap.

The train was evacuated for one hour before gas generation was commenced, the glycerol bath on A being heated to 150°C. during the evacuation. Gas generation was

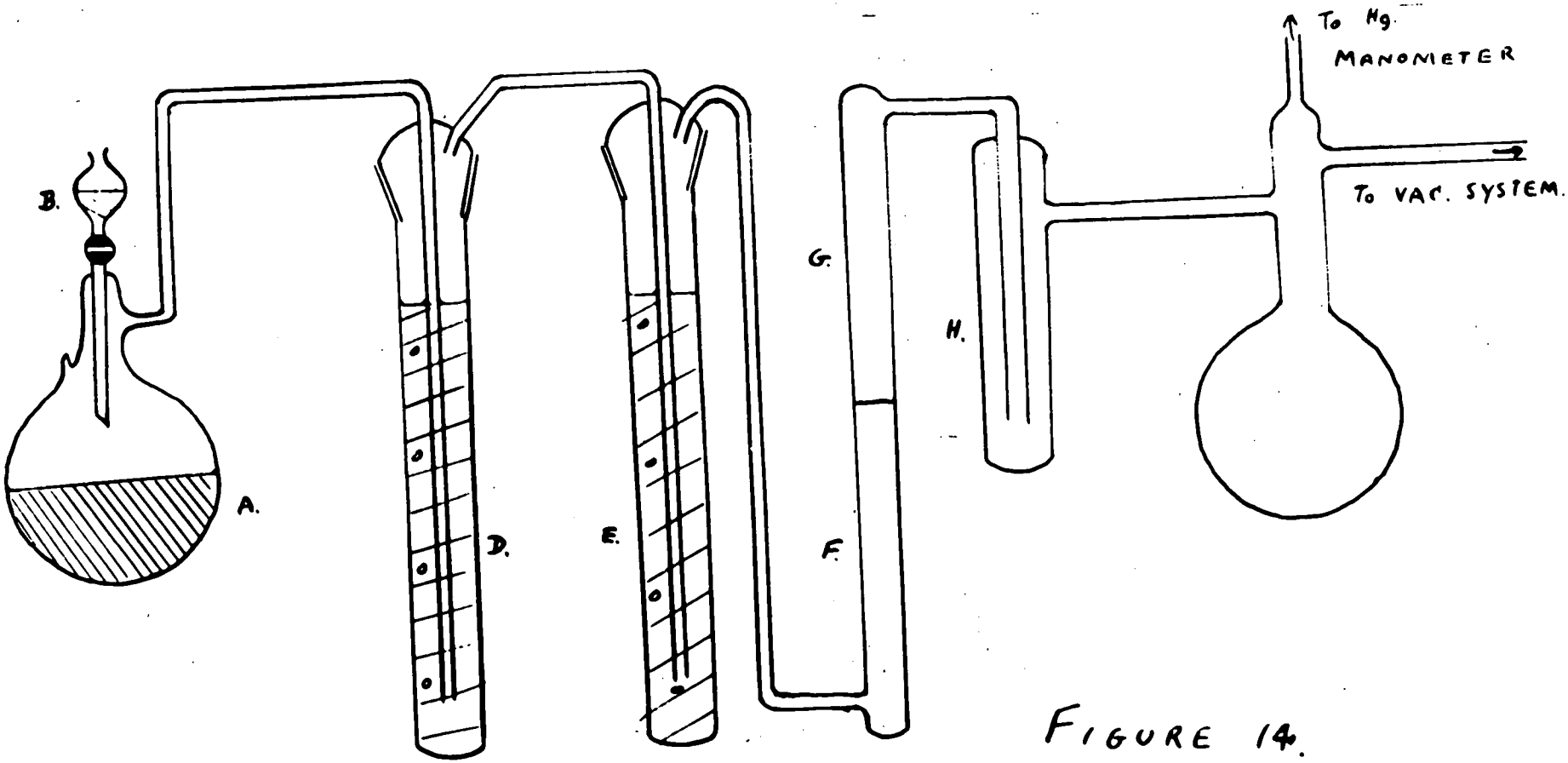


FIGURE 14.

then commenced and the pressure allowed to build up to about 20 cms.Hg. This flushing gas was then pumped away and the generation continued until the storage bulb was filled to a pressure of about 70 cms.Hg. The only impurities leaving A in the carbon monoxide are carbon dioxide, acid spray and a little air. The adsorption towers will remove the carbon monoxide, acid spray and moisture together with the trace of oxygen present from the dissolved air.

4. Inert Gases:-

Krypton and argon were supplied in sealed flasks from the British Oxygen Company Ltd. They were labelled spectroscopically pure.

5. Oxygen:-

This was prepared as described in Section II by the thermal decomposition of potassium permanganate.

(b) Apparatus

The adsorption apparatus, a photograph of which is given in fig. (15), was almost identical to that used in the kinetic studies. As indicated in fig.(9) two gas burettes were incorporated in the system. During kinetic measurements burette B_1 was isolated, all measurements being done with burette B_2. However, in the surface area measurements burette B_2 was isolated.

Burette B_1 consisted of six bulbs joined by short lengths of capillary tubing, mounted vertically in order of

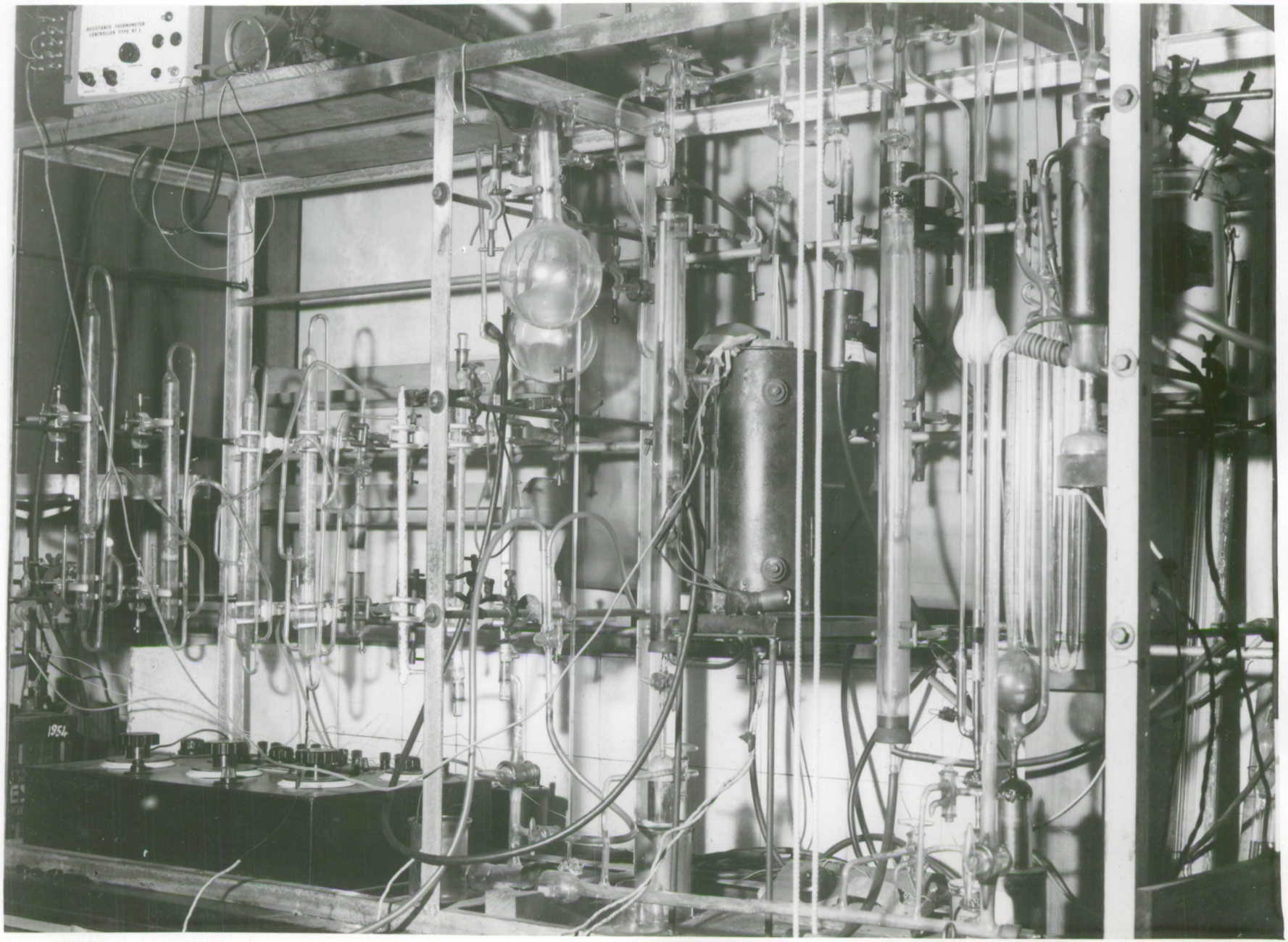


FIGURE 15a

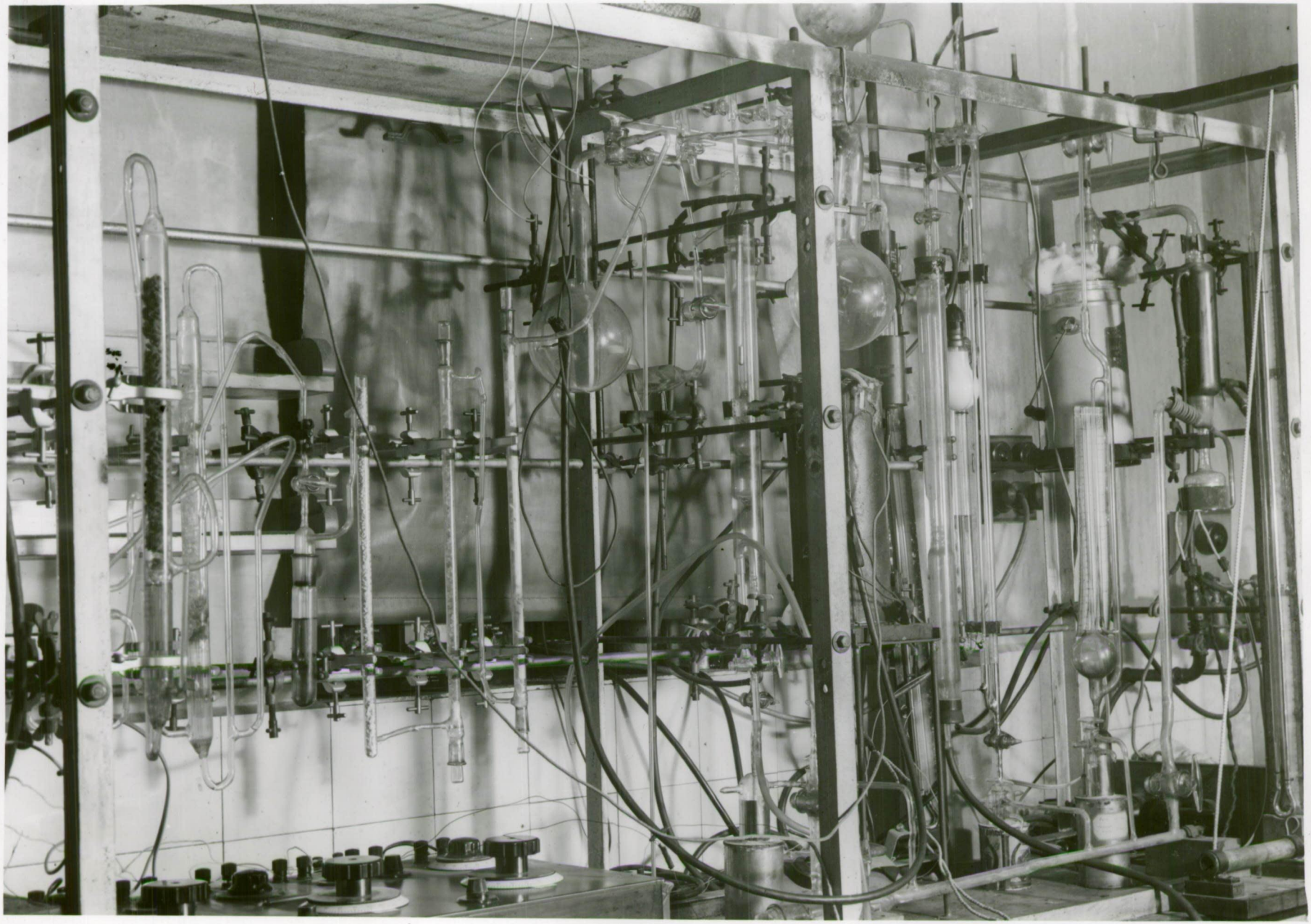


FIGURE 15b.

decreasing volume, the whole being water jacketted. The volume of each bulb was determined before attaching to the apparatus by weighing the volume of mercury it contained. Duplicate measurements of the volume of each bulb agreed to 0.005 ccs.

The mercury manometer, with platinum contacts C_1 and C_2, has been described previously. The level in the manometer was adjusted so that the mercury in the left hand arm was just touching the upper contact (C_1). The difference in height of the two arms was measured by means of a cathetometer. The average deviation of a given height when a series of readings were taken was found to be less than 0.005 mm. The apparatus is similar to that described by Harkins (74) differing only in the manometer arrangement.

The volume of the tubing connecting the burette and the adsorption bulb was determined by measuring the change in pressure in the system when successive bulbs in B_1 were filled with mercury from the reservoir. For one system the volume of the tubing was 16.25 ± 0.05 ccs.

The dead space in the adsorption bulb was doubly checked. It was first determined by measuring the drop in pressure in the system when nitrogen was allowed to expand into the bulb. It is more usual to use helium as the expanding gas but this was not available. It was felt that the use of nitrogen was open to error owing to the possibility of chemisorption at room temperature. As a second check the dead space was

measured by cutting down the evacuated bulb above tap T_1, weighing, filling with water and reweighing. From the increase in weight the volume of water filling the dead space was calculated. The two measurements were in good agreement.

(c) Procedure for Nitrogen

The adsorption bulb, sealed to the end of capillary tubing, was filled with nickel oxalate using the glass bead technique previously described. The tube was sealed to the apparatus at point X in fig. (9). Care was necessary in the initial evacuation of the bulb to prevent the powder blowing up into the capillary.

The sample was outgassed for two hours at room temperature and then the furnace described in Section II was placed in position and its temperature controlled to 210°C. Dehydration of the sample was allowed to proceed for twentyfour hours, after which time the temperature was increased to 330°C. and decomposition allowed to continue for a further twentyfour hours, this time usually being sufficient for complete decomposition.

The adsorption bulb was immersed in a large dewar vessel containing liquid oxygen and two hours allowed to elapse for thermal equilibrium to be established. Taps T_2, T_3, T_5 and T_7 (fig.(9)) were then shut and the mercury adjusted to the mark at the base of the largest bulb in the burette. The

burette system was then filled with nitrogen via tap T_6 to a pressure of approximately 75 cms.Hg. The mercury in the manometer was adjusted until the left hand level was just touching the platinum contact C_1 and the pressure was accurately measured with the cathetometer. Tap T_1 was then opened and mercury forced up into the burette until it was level with the mark at the bottom of the second bulb. At least one hour was allowed to elapse and the equilbrium pressure recorded. The mercury was then forced up into the second bulb, another hour allowed to elapse and a second equilbrium pressure recorded. This procedure was repeated until an equilbrium pressure of 50 cms. had been reached, this being the maximum measurable with the cathetometer.

The liquid oxygen dewar was then removed and the sample evacuated overnight at room temperature. The adsorption measurements were then repeated at -183°C. At the completion of the adsorption measurements the evacuated bulb was cut down, filled with water and from the increase in weight the dead space calculated.

From the known volumes of -

(a) the bulbs in the burette,

(b) the connecting tubing and

(c) the dead space,

together with the equilbrium pressures it was possible to calculate, from the gas laws, the volumes of nitrogen adsorbed at each pressure. The volumes were not corrected for deviations

from the gas laws as suggested by Brunauer and Emmett (105).

Procedure for Carbon Monoxide

The experimental procedure in the case of carbon monoxide was identical to that described except in one aspect. Carbon monoxide was first admitted to the sample at room temperature. Chemisorption was allowed to proceed and, when complete, the adsorption bulb was evacuated for one hour. The bulb was then immersed in liquid oxygen and the physical adsorption determined as for nitrogen.

Procedure for Inert Gases

Unfortunately the argon storage bulb was broken while attaching to the apparatus. Rather than delay the surface area measurements while waiting for a replacement it was decided to use krypton instead, a flask of this gas being available.

The saturation vapour pressure of krypton at -183°C. is approximately 20 mm.Hg. (69). In order to obtain experimental data in the range $0.05 < \frac{P}{P_o} < 0.35$ (suitable for B.E.T. plots) it is necessary to measure equilbrium pressures in the range $0.10 < P < 0.70$ cms.Hg. This pressure range is above the upper limit measurable with the pirani gauge available and almost below values which can be measured accurately with the mercury manometer. The McLeod gauge attached to the vacuum system was not suitable to measure pressures higher than 3×10^{-1} mm.Hg.

The solution to the problem was to construct a McLeod gauge of suitable dimensions such that pressure measurements could be made in the desired range. It was decided, however, to defer construction to a later stage. A few measurements, using the mercury manometer as the pressure indicator, were conducted. These measurements, however, lay outside the range suitable for the B.E.T. equation but they were plotted according to the Huttig equation and the surface areas calculated. The experimental procedure was identical to that described for nitrogen.

RESULTS

The results have been divided into two groups. The results in the first group, which are pertinent to the kinetic studies described in Section II, were obtained with nitrogen alone. Those in the second group are for the three adsorbates studied on the same adsorbent sample.

Table (6) gives the results of the first group and indicates the variation of surface area of the nickel powders with the time and temperature of decomposition of the nickel oxalate.

Table (7) lists the results of the adsorption of nitrogen, carbon monoxide and krypton on a single sample of nickel powder. After these measurements were completed the nickel sample was oxidized at 300°C. and the surface area

measurements repeated. The results of these latter measurements are also recorded in Table (7). In all cases the results given are the average of at least duplicate measurements.

TABLE (6)

Time and Temp. of Decomposition	Weight of $NiO_2O_4 \cdot 2H_2O$	Surface Area $m^2/gm.Ni$.		
		B.E.T.	Huttig	M.J. Relative
15 hrs. at 312°C.	3.906	23.14	23.06	22.44
16 hrs. at 323°C.	4.056	21.60	21.70	21.77
24 hrs. at 330°C.	4.299	16.67	16.50	15.88
24 hrs. at 330°C.	4.115	16.93	16.86	16.29
48 hrs. at 330°C.	10.97	14.71	14.69	14.39

TABLE (7)

-Ni Powders-

	V_m /gm.Ni			Surface Area m^2/gm.Ni		
	B.E.T.	Huttig	A	B.E.T.	Huttig	M.J. Rel.
N_2	3.09	3.10	120	14.71	14.76	14.39
CO	3.27	3.30	160	14.28	14.41	14.69
Kr	-	3.29	-	-	19.21	-
66	-Ni O Powders -					
N_2	2.35	2.33	83	11.19	11.10	11.18
CO	2.72	2.68	152	11.88	11.70	14.21
Kr		2.28		-	13.31	-

Table (8) gives the values of the constants used in evaluating the surface areas. These values are based on the results of Pickering and Eckstrom (67).

TABLE (8)

GAS	TEMP.	k	σ
N_2	-183	4.33	17.72
CO	-183	4.07	16.25
Kr	-183	6.28	21.73

Fig.(16) and (17) show the Harkins Jura relative and the B.E.T. plots respectively of the results given in Table (6).

Figs.(18), (19) and (20) illustrate some of the B.E.T., Huttig and Harkins Jura plots respectively, corresponding to the results given in Table (7).

DISCUSSION

Examination of Table (6) reveals that the surface area of the nickel powders decreases with an increase in both the time and temperature of decomposition of the parent salt. This change is evident in all three methods and therefore can be accepted without qualification. In the case of the Harkins Jura relative method two linear portions were obtained in the

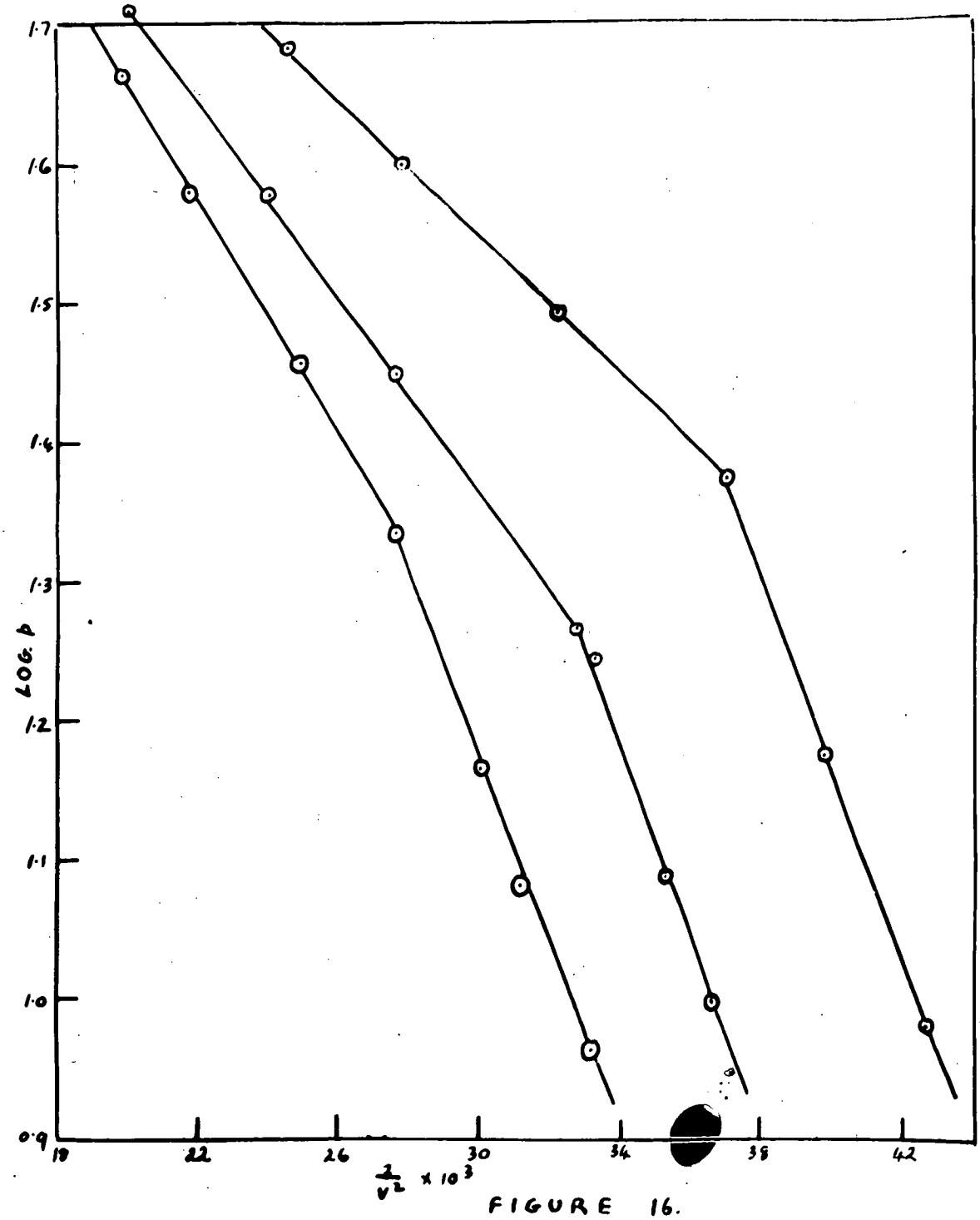

1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
LOG. D
18
22
26
30
34
38
42
$\frac{1}{V^2} \times 10^3$

FIGURE 16.

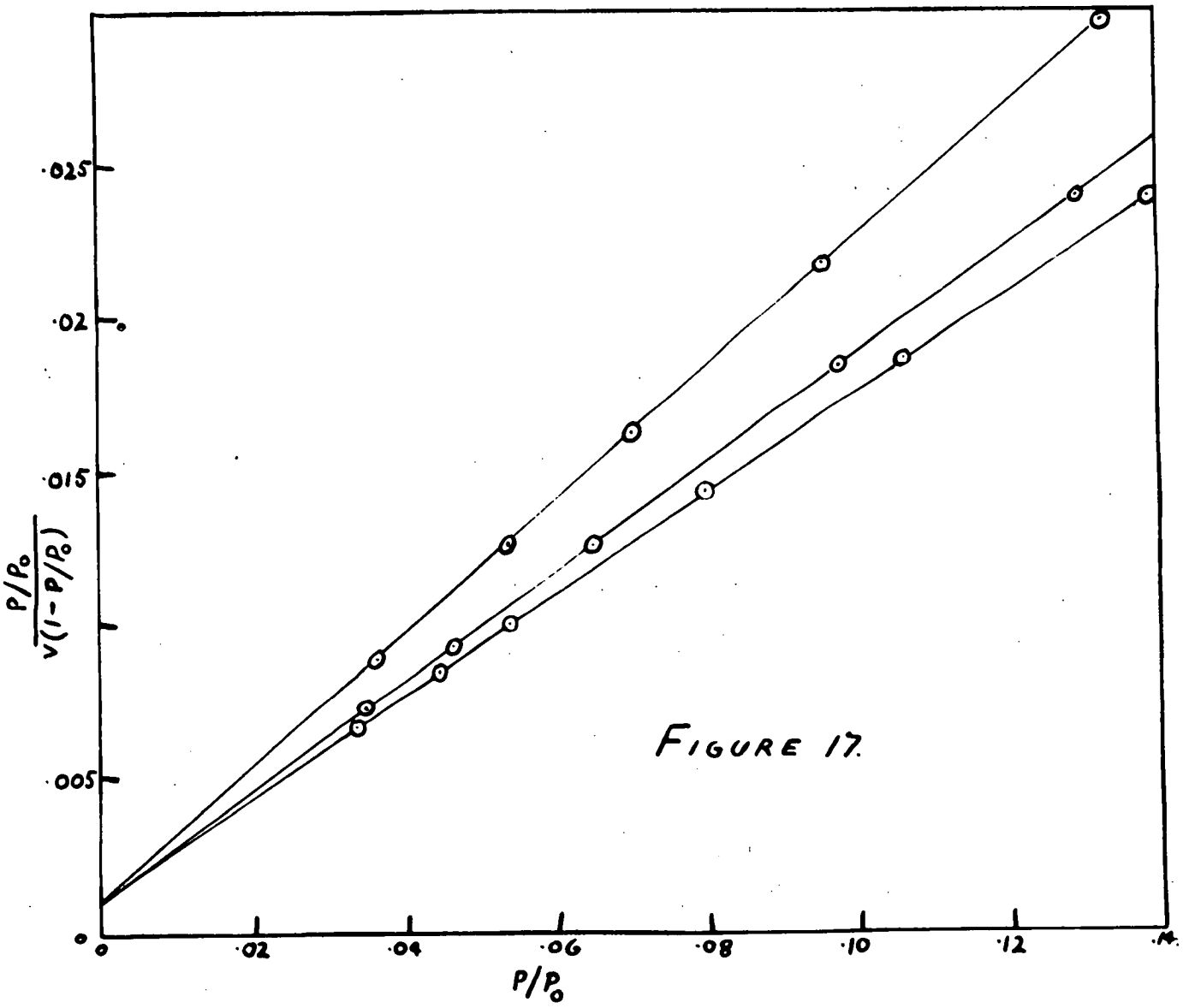


FIGURE 17.

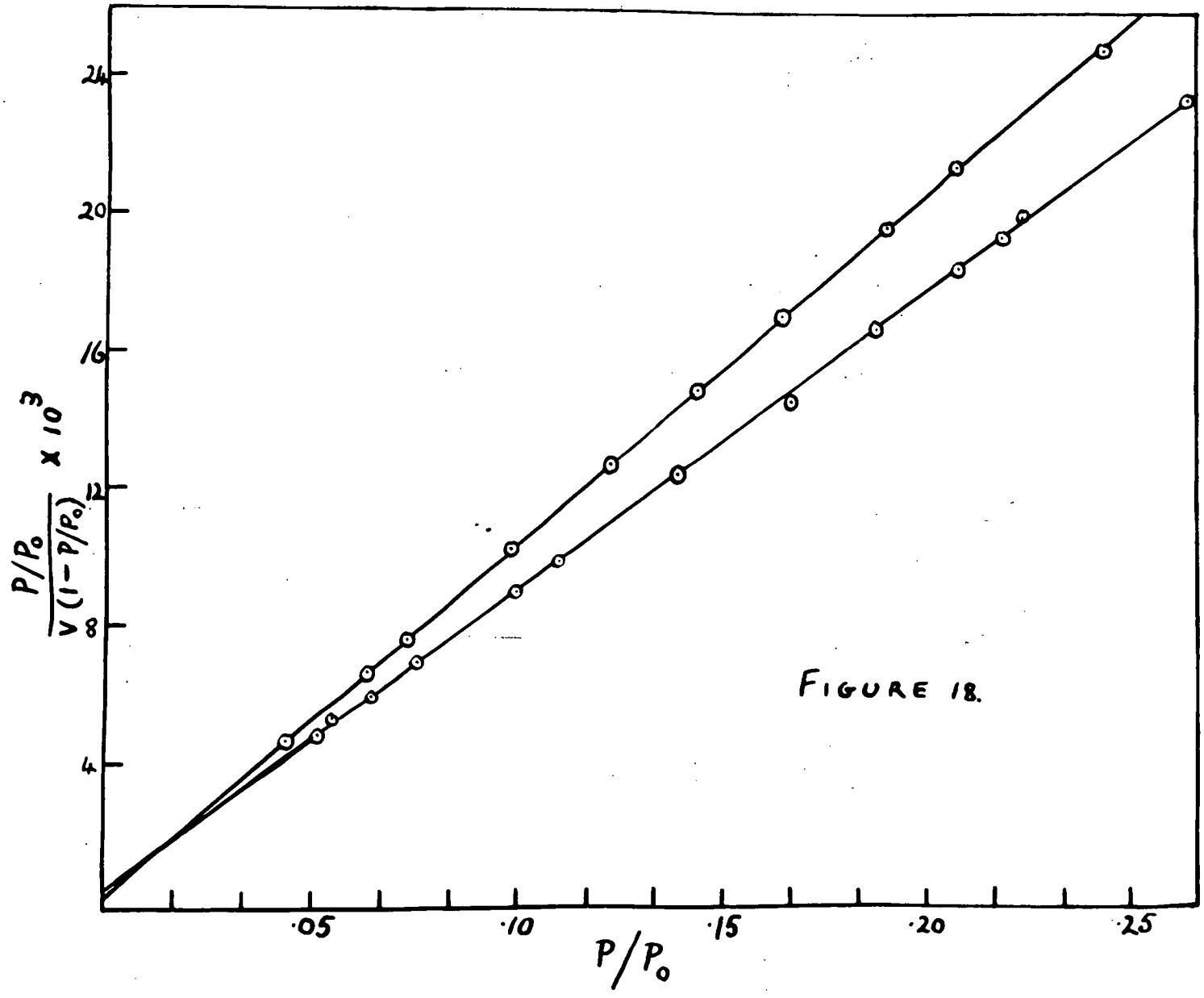


FIGURE 18.

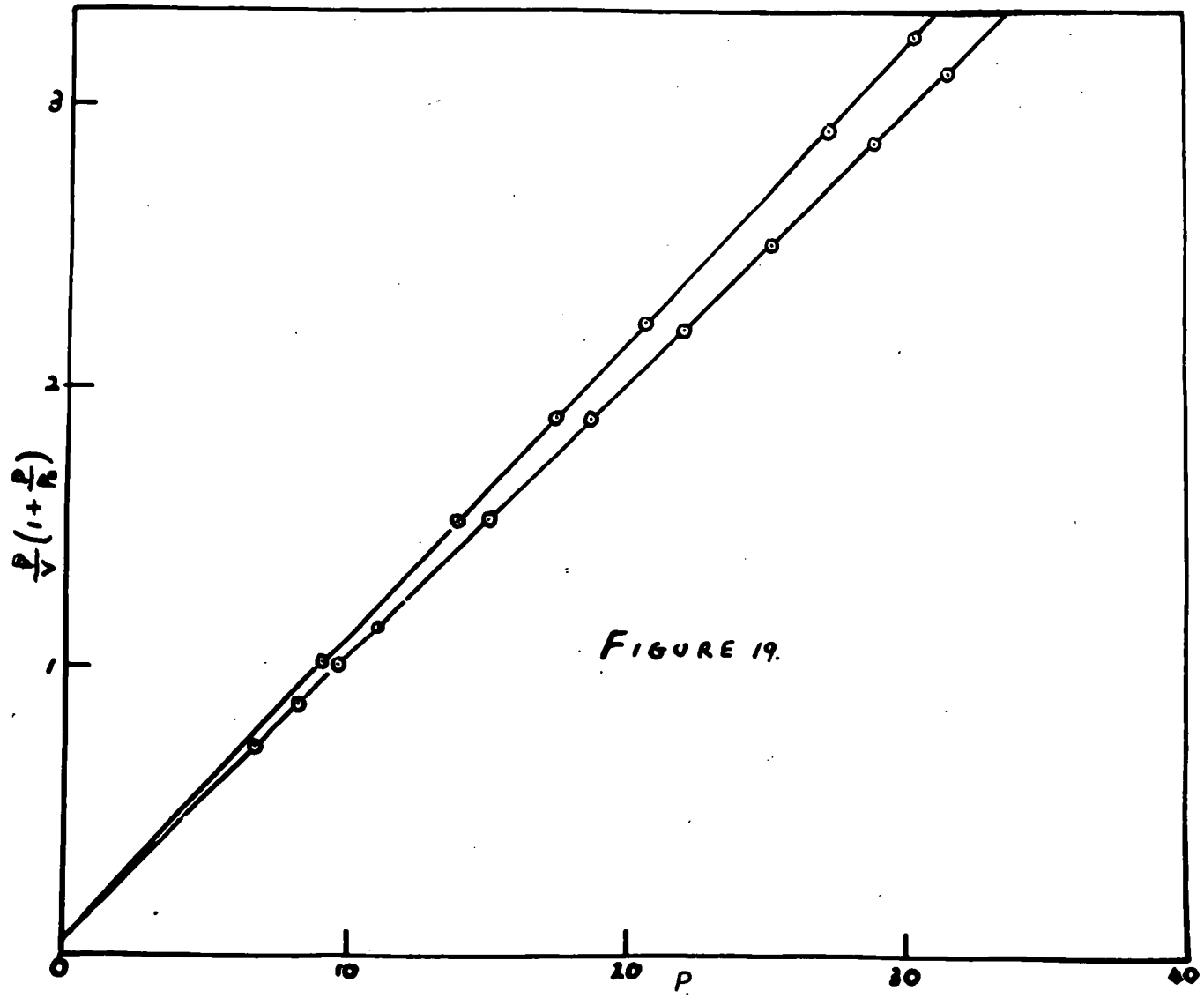


FIGURE 19.

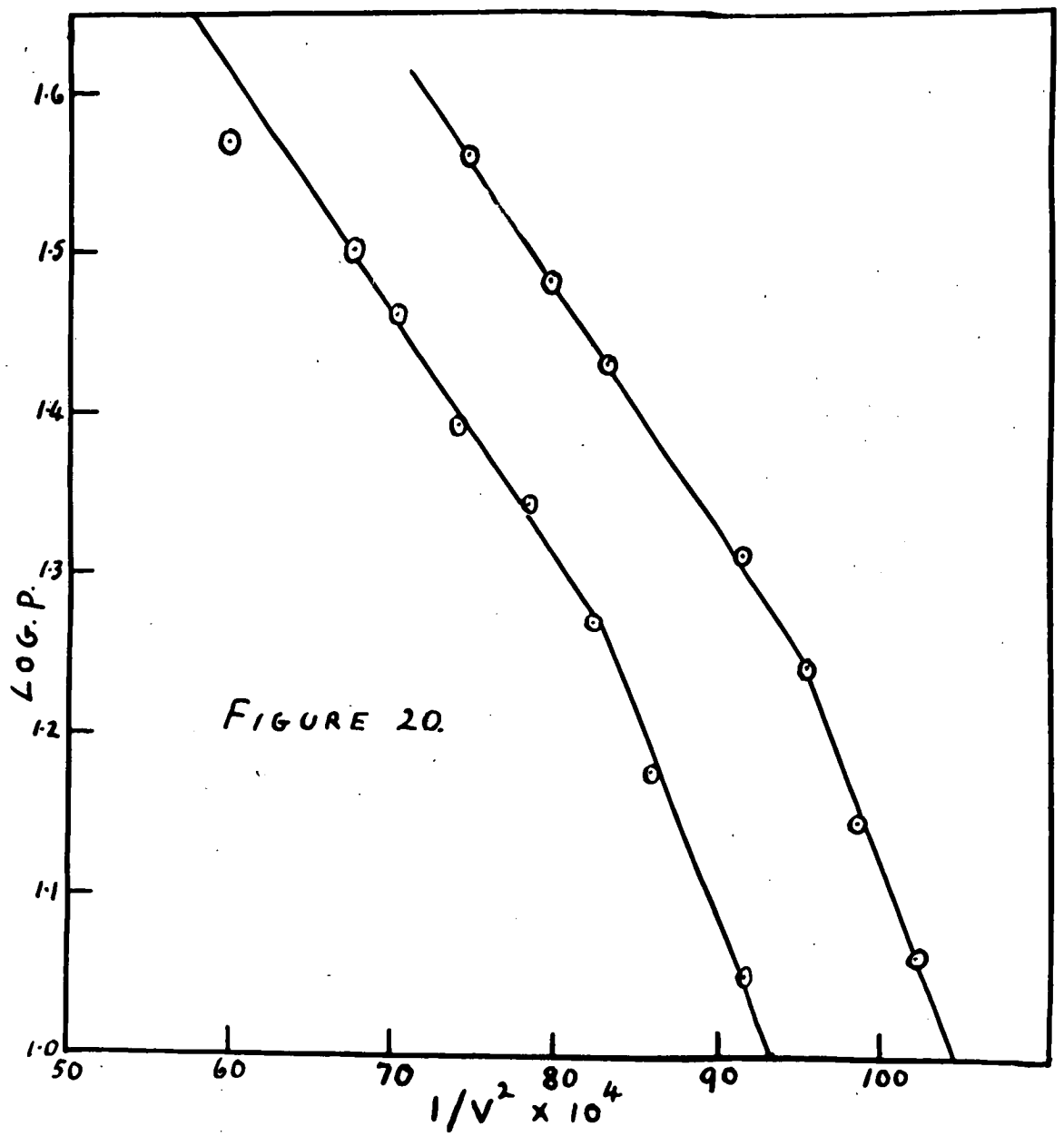


FIGURE 20.

plot log.P $\sim \frac{1}{V^2}$ shown in fig.(16). As suggested by Corrin (89) the slopes which gave the closest agreement with the B.E.T. results were chosen as the correct values. The significance of the variation in surface area with the history of the sample has been discussed previously.

Examination of the results given in Table (7) reveals the following points:-

1. Agreement between the three methods is good.

2. Chemisorption has little effect on the final result provided it is allowed to proceed prior to the low temperature physical adsorption.

3. The krypton results are not in agreement with those of nitrogen and carbon monoxide.

4. The Harkins Jura relative results are the least satisfactory.

5. The surface area of the nickel powders decreased as the result of oxidation.

6. The surface areas values for nickel oxide are somewhat higher in the case of carbon monoxide than the nitrogen values.

7. The agreement between duplicate measurements as shown in fig.(21) is good.

We may examine these points in greater detail.

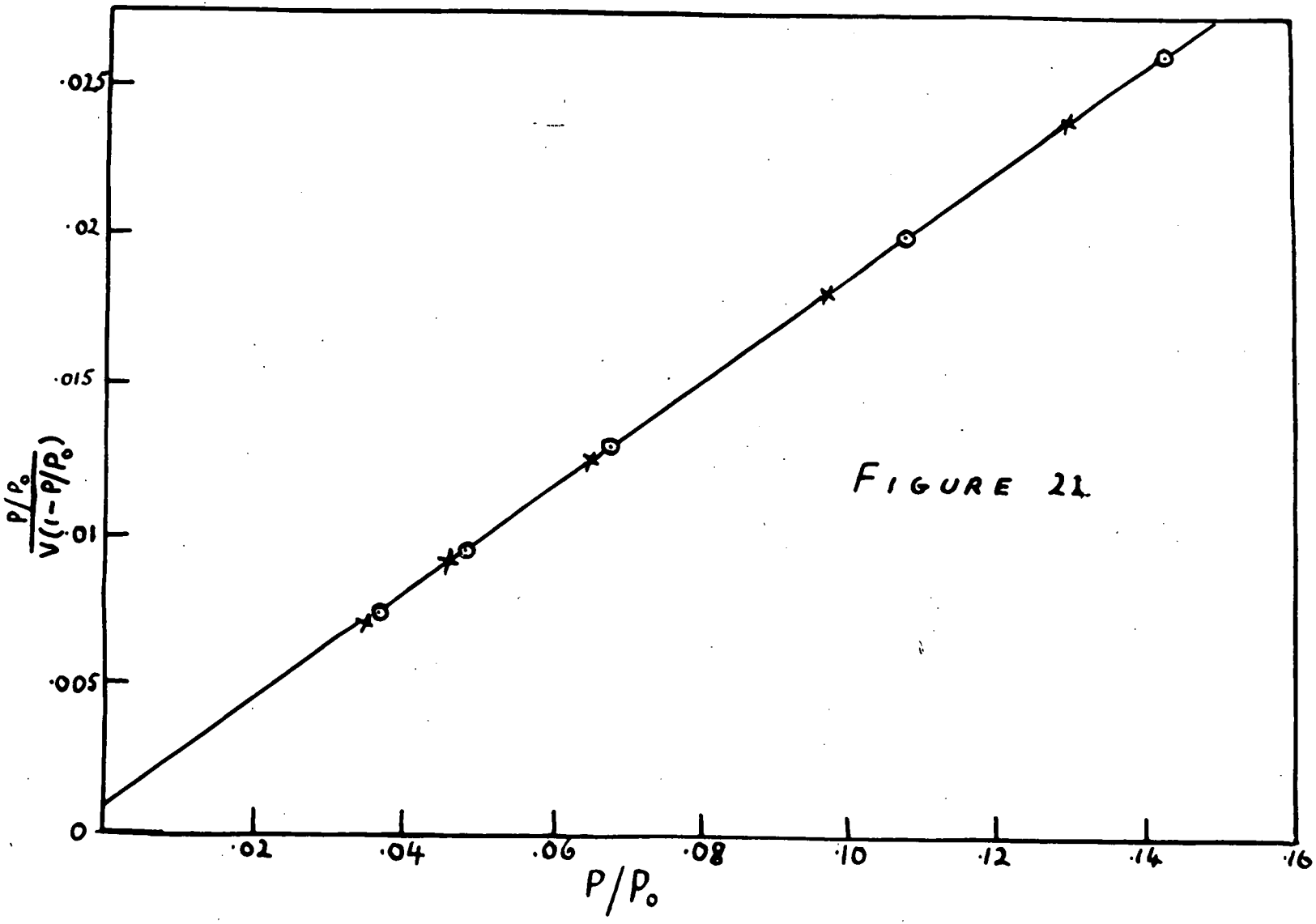


FIGURE 21

1. This result requires little comment as fair agreement was anticipated in accordance with most published work.

2. This result confirms the findings of Brunauer and Emmett (103) on the iron ammonia catalyst. Chemisorption in the case of nitrogen has a negligible effect upon the final result. The error involved in ignoring such chemisorption is probably less than the experimental error.

3. The poor result in the case of krypton may be due to:-

(a) Inaccurate pressure measurements using the mercury manometer. This is supported by the inability to obtain a straight line in the case of the Harkins Jura method. A linear plot in the case of the B.E.T. method was not expected as the pressure measurements were outside the range accepted for the B.E.T. isotherm.

(b) Insufficient time between pressure measurements to allow true equilibrium to be established. The relative pressures used were much higher than those usually accepted and it has been noted by many authors that equilibrium is attained slowly when approaching the saturation pressure.

(c) The value of σ suggested by Pickering and Eckstrom (67) and used in the calculations is considerably larger than the values suggested by either Davis et al (70) or Beebe et al (69). If the value suggested by Beebe et al was used much closer agreement with the other results would be obtained.

4. Of the three methods, that of Harkins and Jura is the least satisfactory. Agreement between different adsorbates is poor and the spread of the points about the straight line (fig.(20)) is greater than either the B.E.T. or Huttig plots. As already indicated there is some doubt in accepting a given value of k as a constant independent of adsorbents. For example Pickering and Eckstrom (67) suggest a value of k = 4.33 for nitrogen at -183 while Joyner and Emmett (93) suggest a value of 4.47.

5. The results clearly indicate that the surface areas decreased as a result of oxidation. This is in contract to that found by Dell and Stone (106) on sintered samples. It is suggested that during oxidation at 300° a certain degree of sintering takes place. This is supported by the earlier results showing a decrease in surface area with prolonged heating at 330°C. Furthermore it is probable that upon admission of oxygen the temperature rise in the sample is considerable, thus enhancing the degree of sintering.

6. The somewhat larger result obtained with carbon monoxide adsorption on nickel oxide may be due to incomplete compensation for chemisorption. It has been shown (107) that the room temperature chemisorption of carbon monoxide is slow. It is probable that insufficient time was allowed for complete equilbrium to be established before proceeding to the physical adsorption.

7. The good agreement between duplicate measurements is a generally accepted fact and needs litte comment.

Before concluding this section a few results of surface area measurements on nickel oxalate dihydrate and anhydrous nickel oxalate are included. These are shown in Table (9) and the corresponding B.E.T. and Harkins Jura plots of some results are given in figs. (22) and (23).

TABLE (9)

SAMPLE	Surface Area $m^2/gm.$ B.E.T.	Harkins/Jura
$Ni\ C_2\ O_4.2H_2O$	1.36	1.30
Anhydrous $Ni\ C_2\ O_4$	107.5 (fig.(22))	114.9 (fig.(23))

The results obtained for nickel oxalate dihydrate are in agreement with values found using air permeability and photo extinction techniques (108). The high value found for anhydrous nickel oxalate is in keeping with surface areas of samples prepared by dehydration of parent salts (107).

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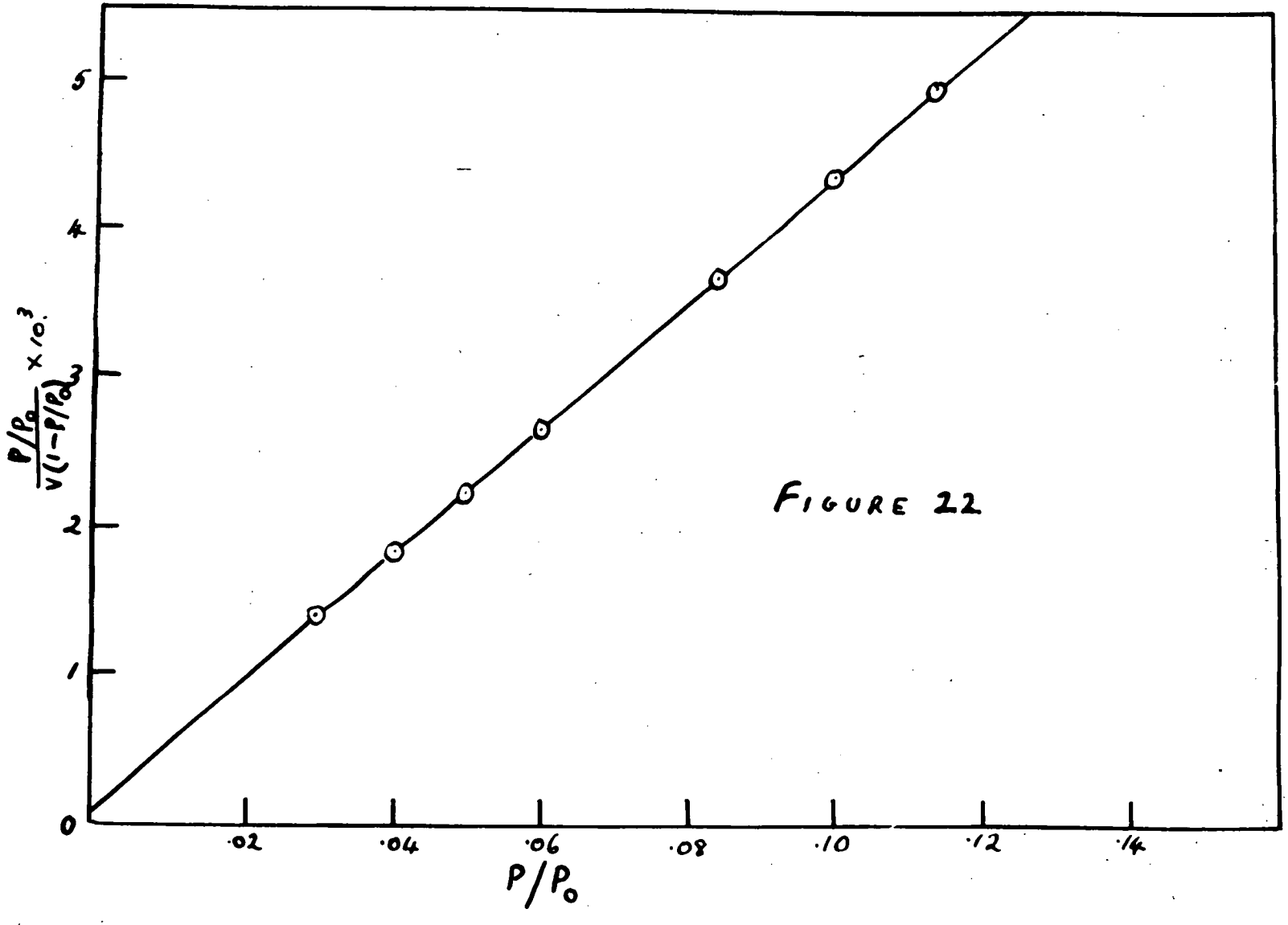


FIGURE 22

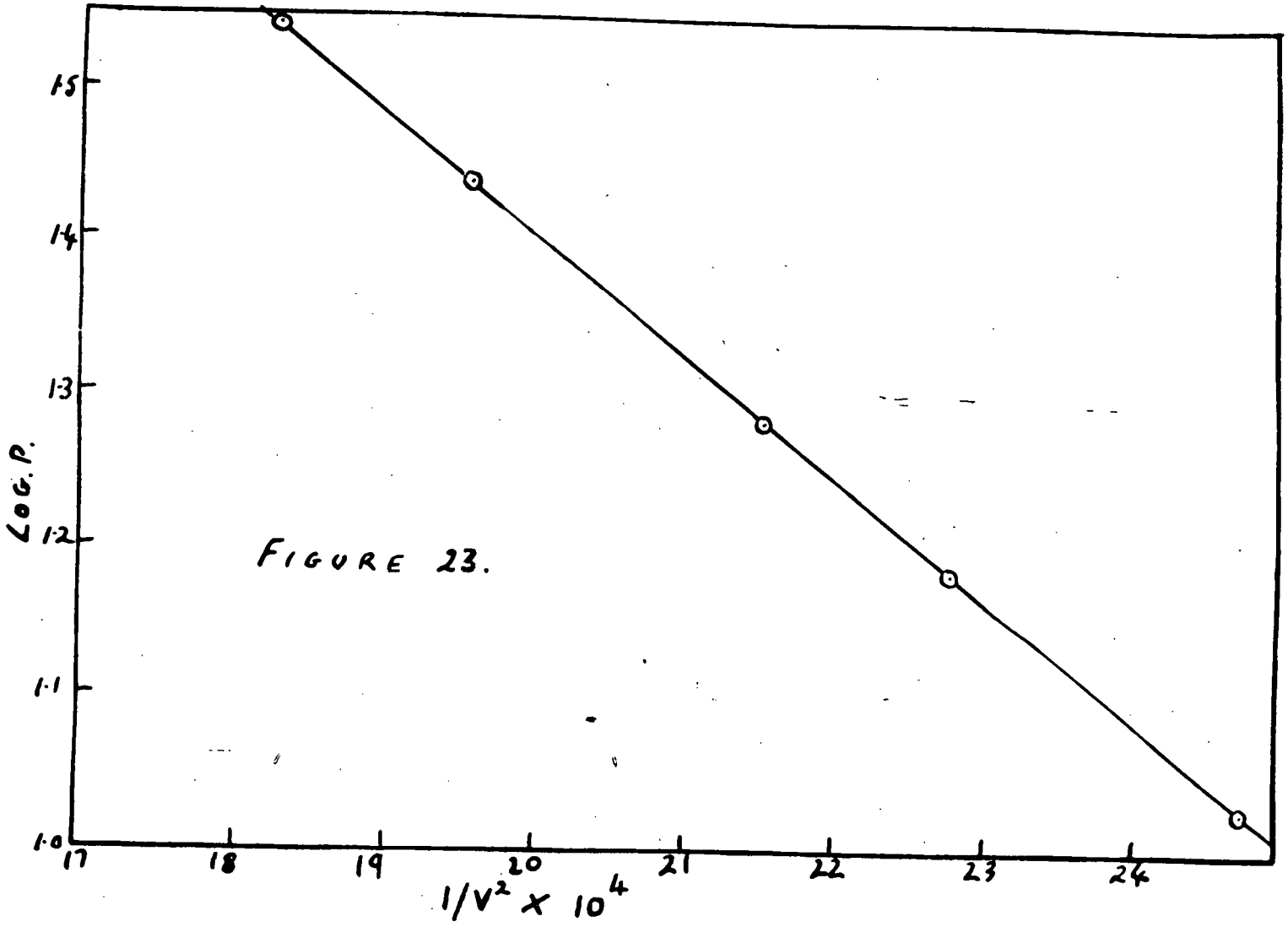


FIGURE 23.

SECTION IV.

SECTION IV

HEAT OF ADSORPTION MEASUREMENTS

INTRODUCTION

In recent years the advances in solid state physics has intensified the research in heterogenous catalysis. The effect of semi-conduction on catalytic activity has received considerable attention and several excellent reviews have been published (109) (110). The adsorption of simple electron donor and electron acceptor gases on transition metal oxides is intimately connected with their semi-conducting properties and hence with catalytic activity.

Recently Teichner and Morrison (107) have investigated the adsorption of oxygen and carbon monoxide on bulk nickel oxide. The results obtained are in contrast with the work of Dell and Stone (106) on nickel oxide films formed on underlying nickel powders. The results are also difficult to reconcile with those of Hauffe and Engell (111) and Krauss (112).

In order that a complete comparison of the adsorption properties of bulk nickel oxide on the one hand and nickel oxide films on the other can be made, it is necessary to possess data on heats of adsorption. The data exists for nickel oxide films (106) but is absent in the case of bulk nickel oxide. The aim of this investigation was to correct this anomaly.

PART I

DESIGN AND TESTING OF CALORIMETERS

LITERATURE SURVEY:

A survey of the literature revealed that both isothermal and adiabatic calorimeters have been used with varied success to measure differential heats of adsorption of gases on powdered adsorbents. The isothermal ones are limited to adsorption at one temperature and the adiabatic type have proved the more popular. This brief review will be confined to adiabatic calorimeters.

The adsorption of gases such as nitrogen, argon and hydrogen at -183 and -195°C. on many finely divided solids has been extensively investigated in recent years (113, 114, 115, 116, 117, 118). It is now generally accepted that differential heats of adsorption fall steadily with an increase in the volume of gas adsorbed. In much of the older literature maxima occur in the curves. These maxima have been attributed to the following:

(a) Poor thermal contact between adsorbent and the temperature sensitive element.

(b) Poor thermal transference through the adsorbent.

(c) Non uniform adsorption.

The last factor is the most serious when differential heat measuremsnts are required, but is not of such importance when a large volume of gas is admitted at one instant and the average

heat of adsorption is recorded.

Two types of errors are encountered in non uniform adsorption. The first type occurs when heat is liberated in a restricted area rather than uniformly. This can be avoided by providing effective means of heat distribution. Alternatively, it may be overcome by having the powder sufficiently dispersed to allow the whole mass of powder to react at the one instant.

The second error arises because of the presence of active centres. If the powder is not sufficiently dispersed, then the first addition of gas will react with centres of differing activity over a limited region, rather than with the most active centres throughout the material. The heats thus measured are then integral heats of successive layers rather than differential heats for the whole sample. The only way in which this error can be eliminated is to have the adsorbent in a layer infinitely thin. The nearest approach to this ideal is in the case of evaporated metal films. In the case of powders the effect can only be minimised by the use of perforated tubes down the centre of the powders or similar methods of increasing the dispersion. Hence, for powders, in the initial measurements of a series, adsorption is probably not uniform and the first values represent integral heats over a limited region rather than differential heats over the whole mass of powder. The initial heats are not entirely due to adsorption on the most active sites and are therefore lower than would be

true if the adsorption process were uniform.

In this regard it is interesting to note that Beeck (113) obtained much higher initial values for heats of adsorption of nitrogen on evaporated metal films than previously found with powders. This was attributed to chemisorption of the nitrogen. It is probable that the lower values obtained with powders were due to non-uniform adsorption which would result in lower initial values but would not greatly effect later values. The lack of cleanliness of the powders compared with evaporated metal films would be a contributing factor.

Several workers have devised calorimeters to eliminate or minimise the effects mentioned.

Bull, Hall and Garner (114) placed the powder in a gauze vessel suspended in a glass bulb. They used a thermocouple placed in the middle of the powder as the temperature sensitive device. The results were found to vary with the depth of immersion of the thermoucouple (115). In later experiments the gas distribution was improved by incorporating a central gauze tube.

Beebe and Wildner (116) have investigated the variation in the heat of adsorption with the depth of immersion of the thermocouple. As a result of this investigation, together with research extending over twenty years, Beebe and co-workers (117) have developed an adiabatic calorimeter which eliminates as far as possible errors involved in earlier designs. The powder is

placed in a silver container to which is soldered a single junction copper constantan thermocouple. The middle of the container holds a perforated platinum tube and to aid heat distribution there are several vertical vanes of copper foil placed inside the silver cylinder. Fine copper shot was intermixed with granules of the adsorbent. The silver cylinder which was joined to the glass inlet tube by a glass to metal seal was completely surrounded by a glass bulb which was continuously evacuated during a heat measurement. Beebe and co-workers have used several calorimeters of this basic design and they work extremely well.

Garner and Veal (119) have devoted considerable time to the study of calorimetry design and the elimination of errors in earlier models. Recently Garner and co-workers (120) have used a calorimeter similar in design to that developed by Beebe (117). The work of Morrison and Los (118) in calrimetry design in recent years has been outstanding. However, the elegant calorimeter used by these workers is beyond the technical capabilities of the Chemistry Department, University of Tasmania and will not be considered further.

Beeck (121) has devised an ingenious calorimeter for heat of adsorption measurements on evaporated metal films. This calorimeter incorporates a platinum resistance winding as the temperature sensitive element. Taylor and Kistiakowski (122) also used a platinum resistance thermometer, but their results were later shown to be incorrect due to poor thermal

contact between the adsorbent and the thermometer. However, most of the more recent calorimeters using powdered adsorbents use a thermocouple as the temperature sensitive device.

FACTORS ASSOCIATED WITH THE PRESENT INVESTIGATION

With regard to the present investigation it was necessary to design a calorimeter which could be used in the first instant for the decomposition of nickel oxalate and nickel hydroxide. It was hoped to carry out heat of adsorption measurements at -183°C. as well as 20°C. Therefore, the calorimeter would have to withstand temperatures in the range -183° to 300°C. It was desirable to use a calorimeter of the Beebe design (117) because these have been shown to work extremely well.

The great disadvantage of such calorimeters lies in the glass to metal seals. In the absence of experience in the fabrication of such seals it was decided to dispence with this complication and to construct the inner calorimeter bulb of glass.

This procedure immediately raised the problem of where or how to place the thermocouple. It could not be attached to the outside of the inner bulb because of the decrease in sensitivity, due to poor conductivity through the glass. The bare thermocouple could not be immersed directly into the powder because of the possible reaction with the adsorbates and also the conductivity of the powders. An alternative lay in the construction of a thin walled pyrex finger dipping into the

the powder and sealed through the calorimeter bulb.

However, the major objection to the use of thermocouples lies in the reduced sensitivity at -183°C. In the case of the Beebe type calorimeter this is partially compensated by the increase in conductivity and reduction in heat capacity of the metal cylinder. However, these effects are not of the same magnitude in the case of pyrex glass.

Another objection to the type of calorimeter used by Beebe and co-workers is the introduction of foreign material such as copper foil and shot. These materials were introduced primarily to transfer heat from the granules of the adsorbent to the metal cylinder and thus to the thermocouple. In the absence of a metal cylinder the presence of this foreign material is not of such importance.

Calorimeter Designs:-

Three calorimeter models were constructed. They were of similar design having a platinum resistance winding as the temperature sensitive element. Each calorimeter was tested in turn by measuring the heat of adsorption of nitrogen on nickel powders at -183°C. As a result of these tests a fourth calorimeter was constructed, but this will be discussed in Part II of this section.

Calorimeter No. 1.

This calorimeter is illustrated in Fig. (24a). It

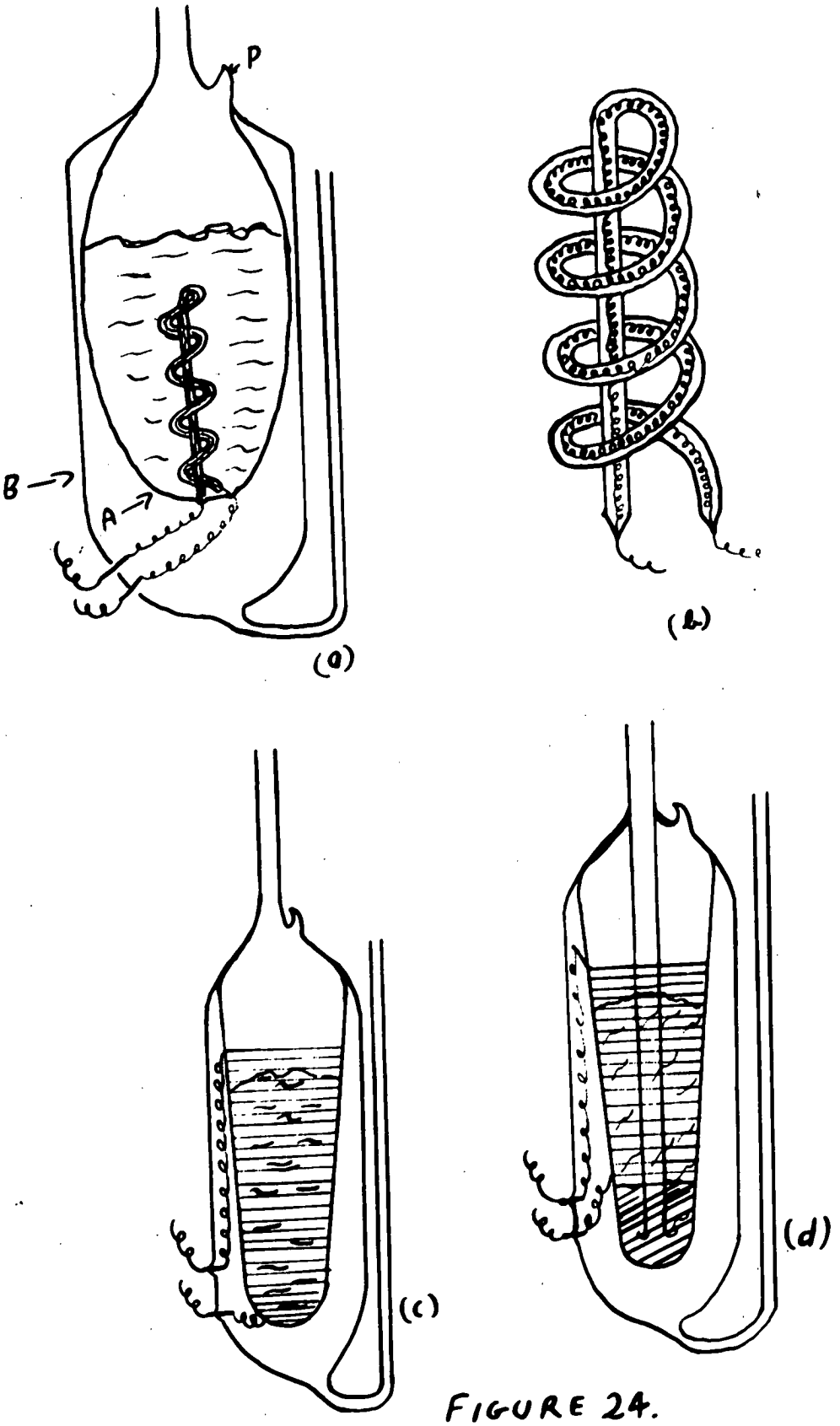


FIGURE 24.

consisted essentially of two bulbs, A and B. Bulb A, which was thin walled, was sealed to the end of the capillary inlet tube and housed the adsorbent. Bulb B, which surrounded bulb A, was continuously evacuated during a heat measurement.

The platinum resistance thermometer consisted of 0.004 inch. diameter platinum wire wound in the form of a long fine coil. The coil was threaded through a very thin walled glass tube which was then bent in the form of a spiral fig. (24b). The spiral was sealed into bulb A and the platinum leads sealed directly through the walls of both bulbs. The adsorbent was placed in the calorimeter via pip P.

Calorimeter No. 2

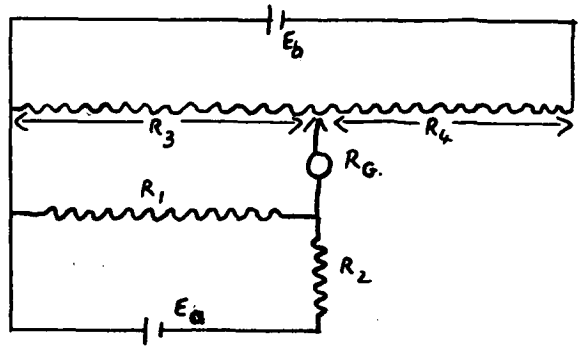
This calorimeter illustrated in fig.(24c) was similar in design to that used by Beeck for evaporated metal films (121). The platinum wire wound around the outside of the inner bulb was held in position by a coating of sodium silicate.

Calorimeter No. 3

The essential difference between this calorimeter, shown in fig. (24d), and No. 2 was in the central inlet tube. The gas entering the calorimeter travelled down the tube, passed through a plug of glass wool at the bottom and then travelled up through the adsorbent. The force required to send the gas up through the powder resulted from the dead space vacuum on top of the powder.

Temperature Measuring Device

The platinum leads from the calorimeter were sealed to copper wires leading to a Cambridge Vernier potentiometer. The following circuit was set up -



E_a and E_b are 2 volt batteries.

R_1 is the thermometer resistance coil (40 ohms.).

R_2 is a resistance to regulate the measuring current through the thermometer (500 ohms.).

R_g is the resistance of the short period galvanometer (21 ohms.).

R_3 and R_4 are the arms of the Cambridge Vernier Potentiometer.

The circuit is identical to that used by Beeck (121) except that a variable resistance across E_a was eliminated. The resistance was used to equalize small drifts of the two batteries to allow the same potentiometer setting to be used for all measurements. This was found unnecessary for the present requirements.

Beeck (121) gives the following final equation for calculating the heat of adsorption.

$$H = \frac{60.6\ C\ (R_1 + R_2)\ d}{a\ R_2\ n\ S}$$

where H = heat of adsorption in cals./mole.

C = heat capacity of the calorimeter

n = number of molecules adsorbed $\times 10^{-18}$

a = temperature coefficient of the platinum

and S = the sensitivity of the balanced circuit, i.e. the galvanometer deflection d in m.m. caused by changing the poteniometer 10^{-4} volts off balance.

Such a definition of the sensitivity S is misleading. The following proof of the formulae is given. In this proof S is rigidly defined.

Proof:

Let E volts be the poteniometer reading when the circuit is balanced initially -

$$\text{then } E = \frac{R_1}{R_1+R_2} \cdot E_a$$

Let S' be the deflection (m.m.) of the galvanometer when the balance is shifted by e volts, i.e. when the poteniometer is e volts off balance and reads (E+e) in place of E. Further let k mm/amp. be the sensitivity of the galvanometer.

Now the current which flows as a result of the circuit being e volts out of balance is $\frac{e}{R}$

$$\text{where } R = \frac{R_1 . R_2}{R_1+R_2} + \frac{R_2 . R_3}{R_2+R_3}$$

$$\text{and further } S' = \frac{ke}{R}$$

The potentiometer is again balanced on reading E. The adsorption experiment is performed, heat is evolved and the resistance R_1 increased by ΔR_1. The circuit is out of balance and the current which flows through the galvanometer is given by

$$\frac{E_a R_2 \Delta R_1}{R (R_1+R_2)^2}$$

Now if this flow of current gives a deflection of d m.m. on the galvanometer scale then

$$d = \frac{k.E_a.R_2\Delta R_1}{R (R_1+R_2)^2}$$

$$\therefore \frac{d}{S'} = \frac{E_a.R_2.\Delta R_1}{e (R_1+R_2)^2}$$

$$= \frac{E_a R_1}{(R_1+R_2)} \cdot \frac{1}{e} \cdot \frac{R_2}{R_1} \cdot \frac{\Delta R_1}{(R_1+R_2)}$$

$$\therefore d = \frac{S'E_aR_1}{(R_1+R_2)} \cdot \frac{1}{e} \cdot \frac{R_2}{R_1} \cdot \frac{\Delta R_1}{(R_1+R_2)}$$

$$= \frac{S'E}{e} \cdot \frac{R_2}{R_1} \cdot \frac{\Delta R_1}{(R_1+R_2)}$$

put $S = \frac{S'E}{e}$

$$\text{then } d = \frac{S R_2}{R_1} \cdot \frac{\Delta R_1}{(R_1+R_2)}$$

$$\therefore \Delta R_1 = \frac{d}{S} \cdot \frac{R_1 (R_1+R_2)}{R_2}$$

$$\text{Now } \Delta T = \frac{1}{R_1} \cdot \frac{\Delta R_1}{a}$$

where ΔT is the temperature increase and a is the temperature coefficient of platinum

$$\therefore \Delta T = \frac{d (R_1+R_2)}{S.a.R_2}$$

$$\therefore H = \frac{C.d.(R_1+R_2)}{a.S.R_2}$$

If n = the number of molecules adsorbed then the heat evolved per mole of gas is

$$H = \frac{6.06 \times 10^{23} \, C \, d \, (R_1+R_2)}{a.S.R_2.n}$$

W.N.D.

This formulae is exactly equivalent to that given by Beeck except that the sensitivity is fully defined and unambiguous.

Such a circuit has several advantages.

1. It is extremely sensitive.
2. The poteniometer need not be standardized against a standard cell.
3. E_a and E_b can be any batteries within a safe range and do not have to be equal.

In order to take a measurement the following procedure was adopted.

1. Balance the poteniometer so that the galvanometer deflection was zero.
2. Admit the adsorbate noting the time.
3. Record the galvanometer deflection every 10 seconds.
4. Plot galvanometer deflection against time and extrapolate back to zero time.
5. Check the sensitivity of the circuit by putting the poteniometer 2×10^{-5} volts out of balance and noting the galvanometer deflection.

Fig.(25) is a typical galvanometer deflection plot.

This method of measuring the heat of adsorption was sensitive and satisfactory. In later experiments average rather than differential heat measurements were made.

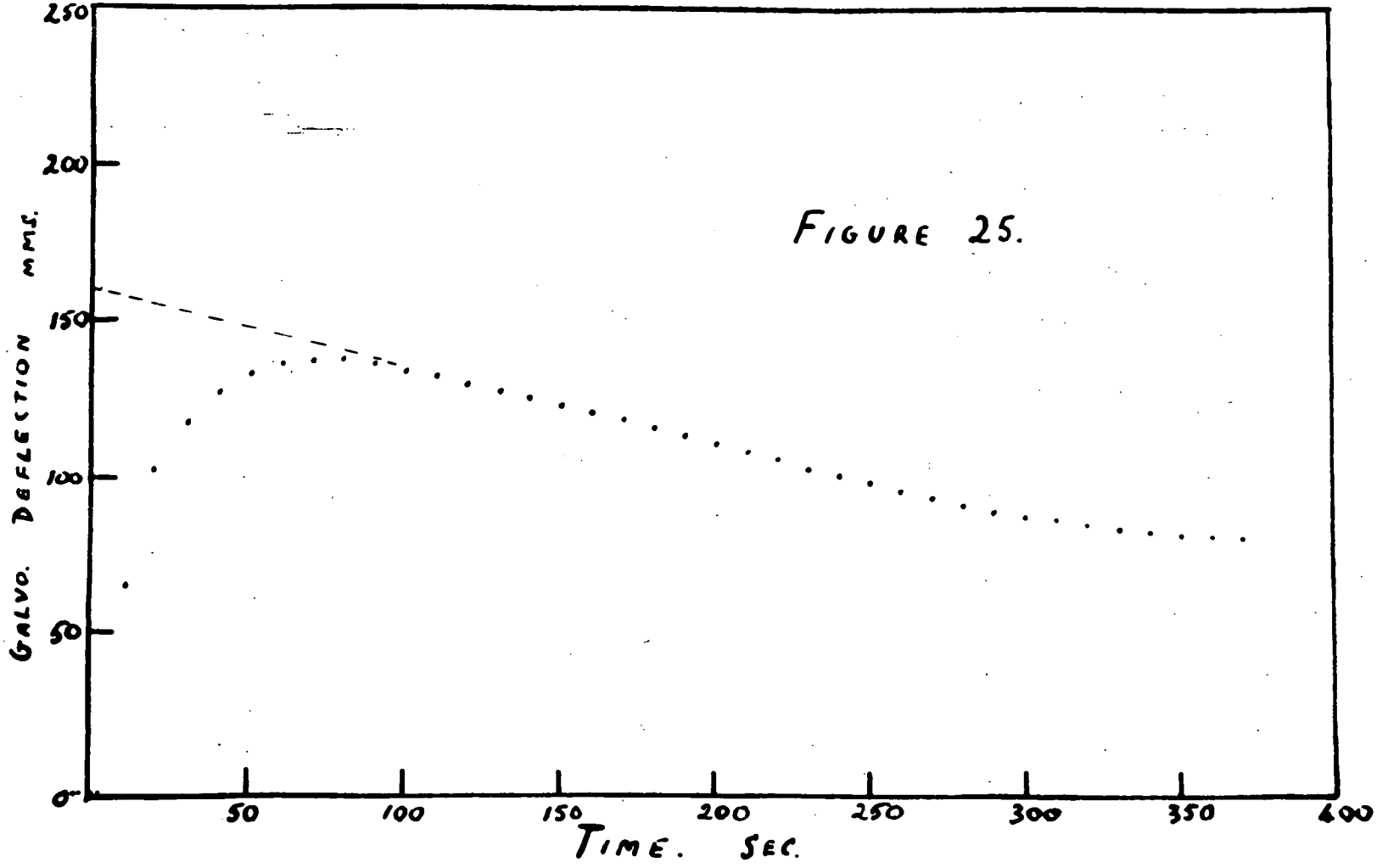

250
200
150
100
50
0
GALVO. DEFLECTION MMS.
50
100
150
200
250
300
350
400
TIME. SEC.

FIGURE 25.

In such cases a larger volume of gas was adsorbed and the heat evolved was considerably larger. In such experiments it was found impossible to keep the galvanometer deflection on the scale without altering the poteniometer setting. Therefore instead of recording the galvanometer deflection with time it was found more convenient to record the poteniometer reading required to keep the galvanometer deflection on the zero mark. This poteniometer reading was plotted against time, extrapolated to zero time and the difference between extrapolated and initial reading calculated. This difference in volts x 10^{-5} was multiplied by the galvanometer deflection caused by changing the poteniometer reading 10^{-5} volts off balance. Thus the actual procedure in recording the increase in resistance of the platinum winding was the same in principle as before except that the sensitivity was reduced. Fig.(26) is a typical plot of poteniometer setting against time. The graph is similar to that shown in Fig.(25) and was easily extrapolated back to zero time.

At -183°C. this method of recording the heat of adsorption was entirely satisfactory. However, at 20°C. some difficulty was encountered owing to the heating effect of the measuring current.

For example with calorimeter No.4 a negative heat of adsorption was recorded when nitrogen was admitted to the evacuated sample. This anomalous result can readily be

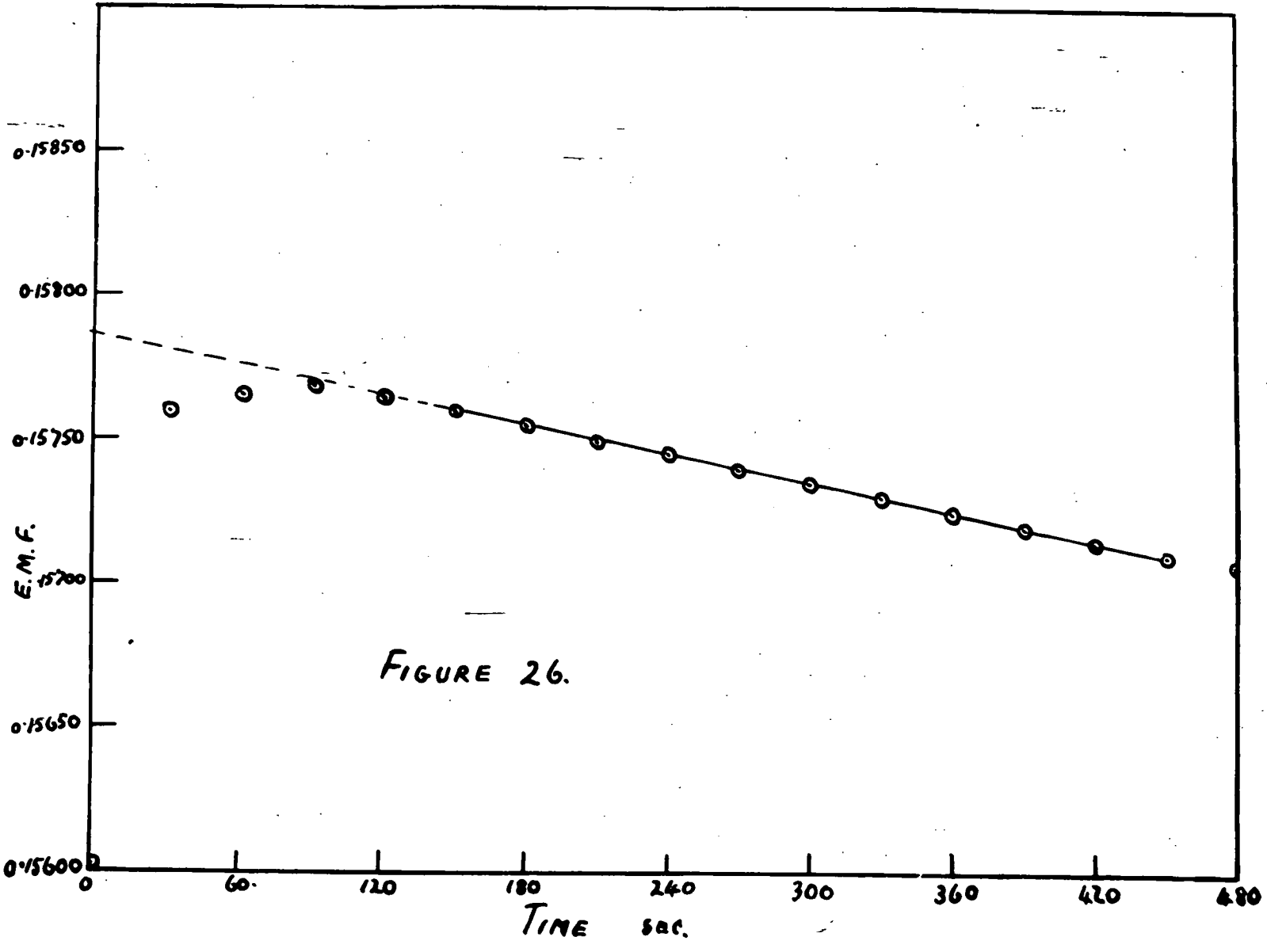

0·15850
0·15800
0·15750
0·15700
0·15650
0·15600
E.M.F.
0
60
120
180
240
300
360
420
480
TIME sec.

FIGURE 26.

explained. Before admission of the nitrogen thermal equilibrium exists in the calorimeter. A steady state is reached in which the rate of heat loss from the inner calorimeter bulb is exactly counteracted by the heating effect of the current flow through the platinum winding. Upon admission of nitrogen the thermal conductivity of the mass of powder is increased. Thus the rate of cooling is enhanced but the rate of energy dissipation from the current flow is constant. Therefore, the temperature of the powder will decrease until a new equilibrium is established. This lowering of the temperature causes a decrease in the resistance of the platinum which is interpreted as a negative heat of adsorption.

In order to overcome this effect a tapping key was placed in the circuit to prevent the flow of current when measurements were not being taken. When taking a measurement the circuit was momentarily closed and the galvanometer deflection noted. This measure was most effective in controlling the heating effect and no further trouble was encountered.

Heat Capacity of the Calorimeter

The heat capacity C can be calculated from the known weights of materials comprising the calorimeter. This was the method used by Beeck (121). However, in the calorimeters used in this investigation it is impossible to

know how much of bulb A is involved in the temperature increase. An approximation can be made, but the final result may be in error.

Wahba and Kemball (123) have used the platinum resistance wire as a heater to calculate the heat capacity of a calorimeter similar to that used by Beeck (121).

However, these authors used a different circuit to measure changes in resistance of the platinum winding.

The following is a proof of their method modified to suit the present circuit.

PROOF:-

It has already been shown (page 11) that

$$\Delta T = \frac{d\,(R_1+R_2)}{R_2 \cdot a \cdot S}$$

therefore if Δx is the galvanometer deflection (using the notation of Wahba and Kemball) corresponding to a change in temperature $\Delta T^{\circ}C$. then

$$\Delta T = \frac{\Delta x \cdot (R_1+R_2)}{R_2 \cdot a \cdot S}$$

$$\therefore \quad \Delta x = \frac{\Delta T \cdot a \cdot S \cdot R_2}{(R_1+R_2)}$$

If the calorimeter is immersed in a thermostat and a constant voltage E applied to the platinum wire, then

after some time a steady state will be reached when the loss of heat from the calorimeter at T_o^o C to the thermostat at T_∞^o C. is balanced by the rate of input of electrical energy.

$$\text{i.e. } E^2/4.18\,R_1 = r(T_o - T_\infty)$$

where E = the voltage, R_1 the resistance of the platinum wire and r = the rate of loss of heat in cals./deg./sec.

After allowing sufficient time for a steady state to be reached the heating current is switched off and the platinum wire switched back to the measuring circuit and the galvanometer deflection followed with time.

Newton's law of cooling states that -

$$\frac{d\theta}{dt} = -k\theta$$

$$\text{i.e. } \theta = \theta_o e^{-kt}$$

where θ = the excess temperature at time t

and θ_o = the excess temperature at time t = o

$$\therefore \theta = T_t - T_\infty$$

and $$\theta_o = T_o - T_\infty$$

$$\therefore (T_t - T_\infty) = (x_t - x_\infty)\frac{R_1+R_2}{a.\ S.R_2}$$

$$\text{and } (T_o - T_\infty) = (x_o - x_\infty)\frac{R_1+R_2}{a.\ S.R_2}$$

$$\text{Now } \ln\theta = \ln\theta_o - kt$$

$$\therefore \ln\frac{\theta_o}{\theta} = kt$$

$$\therefore \ln \frac{(x_o - x_\infty)}{(x_t - x_\infty)} = kt$$
$$= \frac{r}{C} \cdot t$$

where r = rate of cooling in cals./deg./sec.

C = heat capacity in cals./deg.

and t = time whenthe heating current is switched off.

Therefore a plot of $\ln (x_t - x_\infty) \sim t$ should be linear if Newton's Law of cooling is obeyed. The slope of such a line is $\frac{r}{C}$ and the intercept gives $(x_o - x_\infty)$.

$$\text{Now } T_o - T_\infty = \frac{E^2}{4.18\ R_1} \cdot \frac{1}{r}$$

$$\therefore (x_o - x_\infty)\frac{(R_1+R_2)}{R_2 a.s} = \frac{E^2}{4.18\ R_1} \cdot \frac{1}{r}$$

$$\therefore (x_o - x_\infty) = \frac{E^2 . a . s . R_2}{4.18 . R_1 . r . (R_1+R_2)}$$

$$\therefore \frac{C}{r}(x_o - x_\infty) = \frac{E^2 . a . s . R_2}{4.18\ R_2\ r\ (R_1+R_2)} \cdot \left(\frac{C}{r}\right)$$

$$\therefore C = \frac{E^2 . a . s . R_2}{4.18\ R_1\ (x_o - x_\infty)(R_1+R_2)} \cdot \left(\frac{C}{r}\right)$$

All the terms in this expression are known or measurable and therefore C can be evaluated.

If the above expression for the heat capacity is included in the formulae derived for the heat of adsorption then the following expression is obtained -

$$H = \frac{E^2 \cdot 6.02 \times 10^{23}\, d}{4.18\, R_1\, (x_o - x_\infty)\, n} \cdot \left(\frac{C}{P}\right)$$

This expression does not contain, a S or R_2. Thus it is not necessary to know accurately these constants.

Fig.(27) illustrates a plot of $\log.(x_t - x_\infty) \sim t$ for calorimeter No.1. This graph was reproducible and gave a value of C which was in agreement with a value calculated from the weights of materials comprising the calorimeter. This method of evaluating C was good at $-183^{\circ}C.$ but less satisfactory at $20^{\circ}C.$ At this latter temperature difficulty was experienced in adjusting the applied voltage E, so that when the platinum winding was switched back to the measuring circuit no adjustment of the potentiometer setting was necessary to keep the galvanometer deflection on the scale. This difficulty was overcome by making E somewhat larger. When the platinum resistance was switched back to the measuring circuit the potentiometer setting was altered to keep the galvanometer deflection on zero. A plot was made of $\log.(\text{pot.}_t - \text{pot.}_\infty)$ against t where pot. indicates the potentiometer setting required to keep the galvanometer deflection on zero.

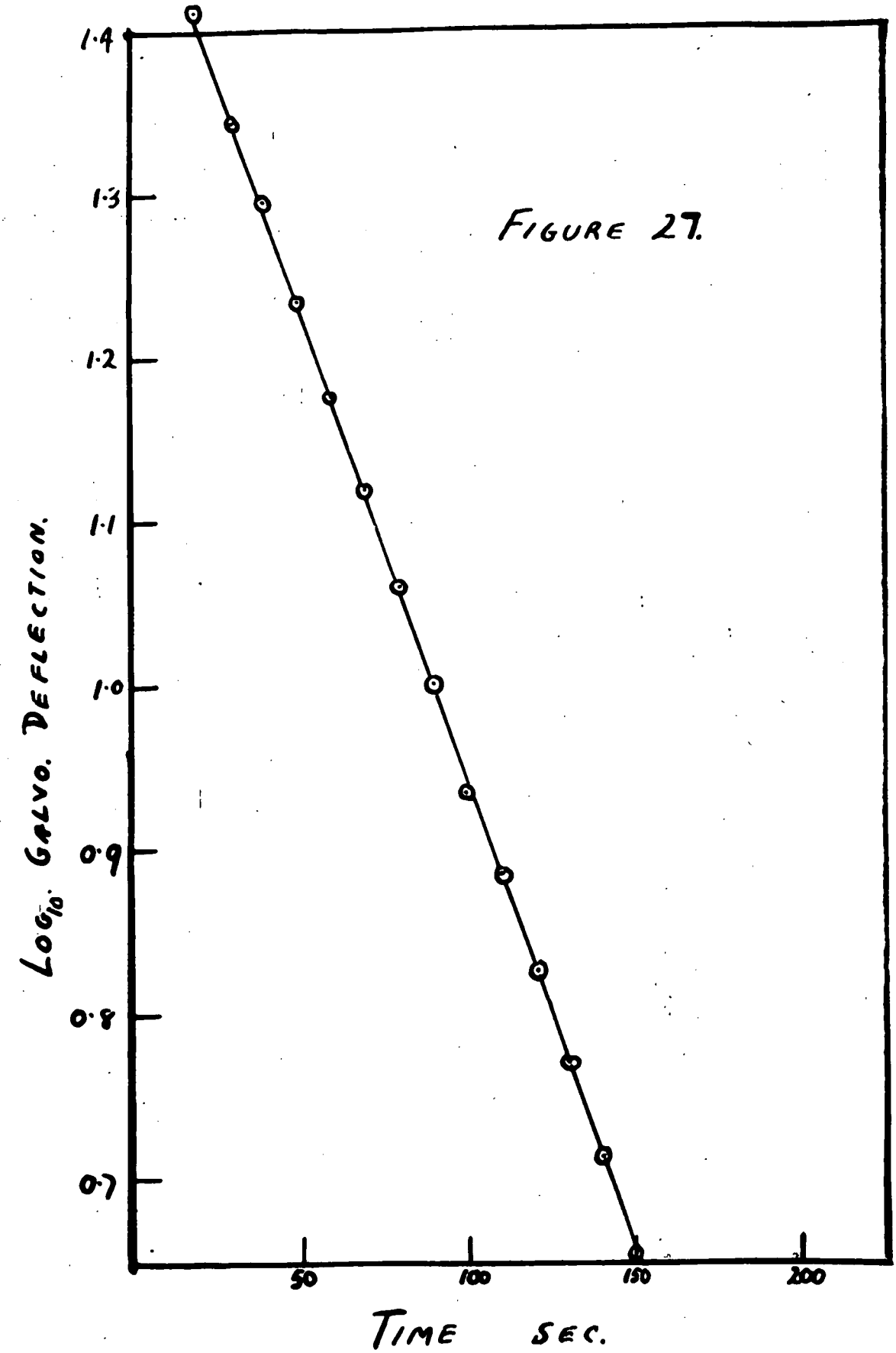

1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
Log_{10} Galvo. Deflection.
50
100
150
200
Time Sec.

FIGURE 27.

Fig.(28) illustrates three typical plots for calorimeter No.4. From the intercept the value of ($pot._0 - pot._\infty$) was calculated. This figure expressed in volts x 10^{-5} was multiplied by the galvonometer deflection caused by putting the poteniometer 10^{-5} volts out of balance and this value was used in the calculation of C. As indicated in Fig. (28) excellent agreement in the calculation of C was obtained for three independent runs.

APPARATUS

The apparatus used was almost identical to that already described in Section III. A minor difference was the inclusion of a Pirani gauge head at a point above tap T_1 in Fig. (9). A large storage bulb and a di butyl phthalate manometer, both of which could be isolated when not in use were attached to the Pirani head. The calorimeters were sealed to the system at point x in fig. (9) in place of the adsorption bulbs.

EXPERIMENTAL

Reagents:-

(1) Nickel Powders:

These were prepared in the calorimeter by the thermal decomposition of nickel oxalate dihydrate. The actual conditions were identical to those previously described.

(2) Nitrogen

This gas was purified as described in Section III.

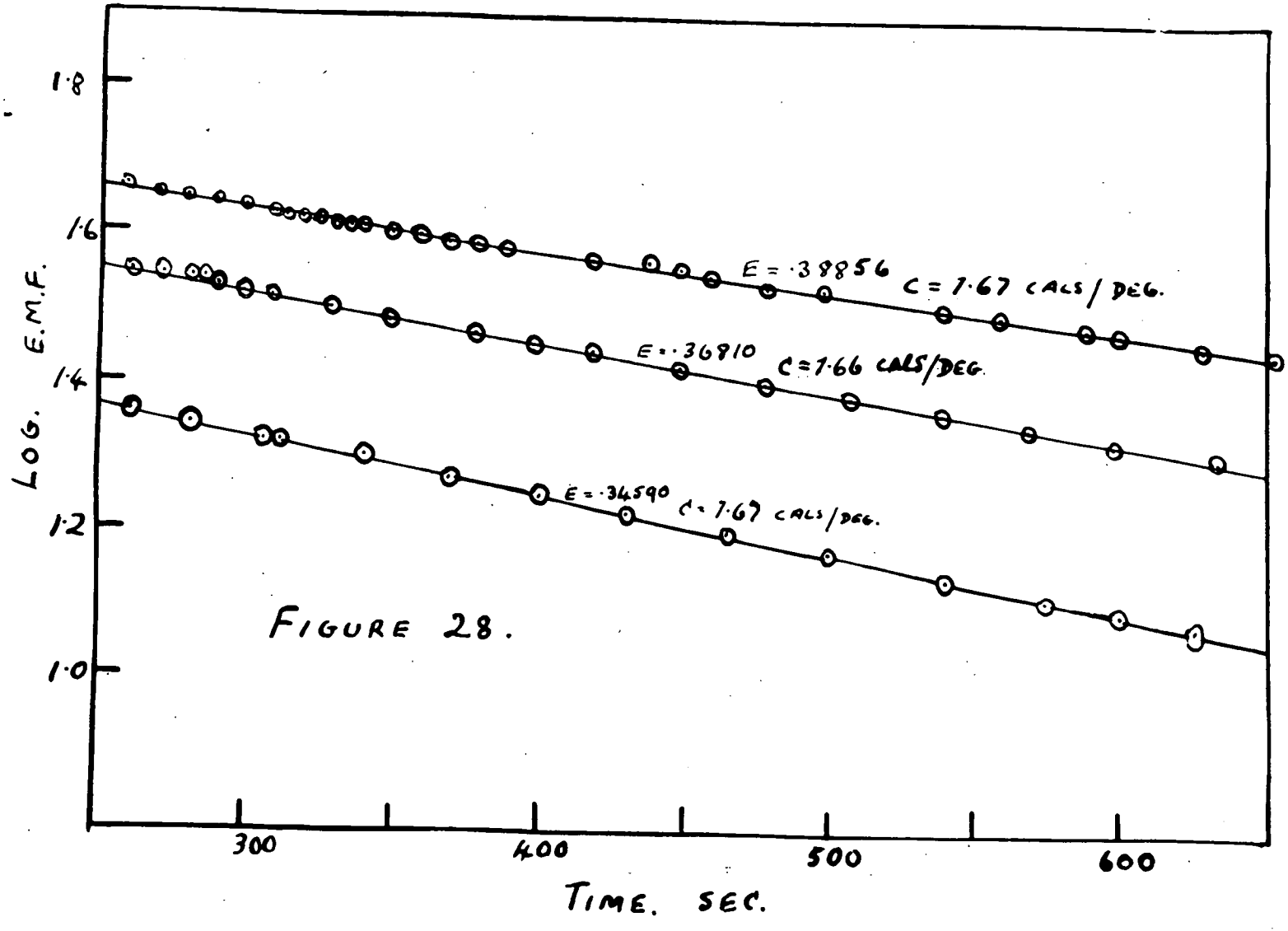

1·8
1·6
1·4
1·2
1·0
LOG. E.M.F.
E = ·38856 C = 1·67 CALS / DEG.
E = ·36910 C = 1·66 CALS/DEG.
E = ·34590 C = 1·67 CALS/DEG.
300
400
500
600
TIME. SEC.

FIGURE 28.

(3) Krypton:

British Oxygen Company labelled spectroscopically pure.

PROCEDURE:

The following is the procedure used to test each of the calorimeters.

A weighed amount of nickel oxalate dihydrate ($\simeq$10 gms.) was placed in the calorimeter through the filling pip P and the calorimeter attached to the vacuum system. The sample was decomposed as previously described and then the calorimeter was immersed in a bath of liquid oxygen. Three hours were allowed to elapse and then the outside bulb B was connected to the vacuum line and continuously evacuated. The Pirani head (volume = 30 ccs.) was filled to a known pressure(0. 5 cms.Hg.) with nitrogen, isolated from the system and this volume of gas admitted to the sample. The galvanometer deflection with time was recorded and a graph drawn. From the extrapolated value the actual heat evolved was calculated. The final equilibrium pressure in the calorimeter was measured with the Pirani gauge. From the known volumes of the bulbs and connecting tubing the volume of gas adsorbed was calculated.

Several admissions of nitrogen were made in this manner. When complete the liquid oxygen was removed, the sample evacuated and then heat of adsorption measurements of krypton at -183°C. were determined in a similar manner.

The equilibrium pressures recorded by the Pirani gauge were corrected for thermomolecular flow where necessary (2). The dead space in the calorimeters was determined by the methods previously described.

RESULTS

1. Calorimeter No. 1 :-

Table (10) lists the heat of adsorption, volume of gas adsorbed and extrapolated galvanometer deflections for nitrogen and krypton on nickel powders. The heat of adsorptions values are plotted against volume adsorbed in fig.(29).

2. Calorimeter No. 2:-

Heat of adsorption results for this calorimeter are listed in Table (11) and plotted in fig.(30).

3. Calorimeter No. 3:-

The results for this calorimeter are given in Table (12) and plotted in fig.(31).

DISCUSSION

Before discussing the results in detail mention will be made of the method adopted to improve the consistency of the results.

Examination of fig.(29) shows that there is considerable scatter of points in duplicate measurements. This scatter may be due to errors in reading the initial pressure in the Pirani bulb with the mercury manometer. A slight error in

TABLE (10)

CALORIMETER NO.1

	Extrapolated Galvanometer Deflection	Volume of Gas Adsorbed $Cms.^3$ S.T.P./Gm.Ni	Total Volume of Gas Adsorbed $Cms.^3$ S.T.P./Gm.Ni	Heat of Adsorption K.cals./mole
N_2	263	1.43×10^{-1}	1.43×10^{-1}	7.75
	184	1.49 "	2.92 "	5.19
	218	1.21 "	4.13 "	7.69
	117	1.08 "	5.21 "	4.73
	100	1.05 "	6.26 "	4.17
	381	3.05 "	9.31 "	5.42
N_2	Repeat			
	200	1.34×10^{-1}	1.34×10^{-1}	6.84
	160	1.32 "	2.66 "	5.35
	104	1.25 "	3.91 "	3.56
	156	1.58 "	5.49 "	4.19
	123	1.31 "	6.80 "	4.17
	80	1.38 "	8.18 "	2.49
Kr	214	1.54	1.54	5.96
	162	1.15	2.69	6.14
	257	1.89	4.58	5.85
	195	2.03	6.61	4.19
	136	1.95	8.56	3.06
	116	1.05	9.61	4.79
	147	1.90	11.51	3.36

Cont..

TABLE (10)

Kr	Repeat			
	138	1.13	1.13	5.09
	78	1.04	2.17	6.48
	196	7.30	3.47	6.50
	236	7.68	5.15	5.74
	170	7.76	6.91	4.04

TABLE (11)

CALORIMETER NO. 2

	Extrapolated Galvenometer Deflection	Volume Gas cms.^{3}S.T.P./Gm.Ni	Total Volume Gas cms.^{3}S.T.P./Gm.Ni	Heat of Adsorption K.cals./mole.
N_2	286	0.241	0.241	2.44
	158	0.144	0.386	2.25
	160	0.139	0.525	2.33
	160	0.135	0.660	2.44
	189	0.129	0.789	3.00
	186	0.124	0.913	3.09
N_2	165	0.128	0.128	2.61
	125	0.124	0.252	2.05
	138	0.119	0.372	2.34
	146	0.116	0.487	2.57
	147	0.110	0.598	2.71
K_2	138	0.172	0.172	1.55
	133	0.166	0.339	1.88
	150	0.164	0.500	1.97
	132	0.151	0.650	1.80
	154	0.150	0.800	2.31
	138	0.144	0.944	2.34
	137	0.138	1.08	2.37
	116	0.133	1.22	2.02

TABLE (12)

CALORIMETER NO. 3

	Extrap. Galvanometer Deflection	Vol. of Gas cms.^{3} S.T.P./Gm.Ni	Total Vol. Adsorbed cms.^{3} S.T.P./Gm.Ni	Heat of Adsorption K.cals/mole
N_2	208	0.127	0.127	3.8
	144	0.109	0.236	3.15
	121	0.104	0.341	2.70
	181	0.101	0.442	4.09
	202	0.099	0.542	4.8
N_2	180	0.132	0.132	3.2
	150	0.131	0.264	2.69
	180	0.128	0.392	3.31
	200	0.123	0.516	3.83
	176	0.121	0.637	3.41
	176	0.118	0.755	3.53
Kr	176	0.254	0.255	1.63
	156	0.249	0.504	1.48
	164	0.243	0.747	1.59
	209	0.237	0.984	2.03
	228	0.226	1.211	2.38
	252	0.224	1.43	2.66

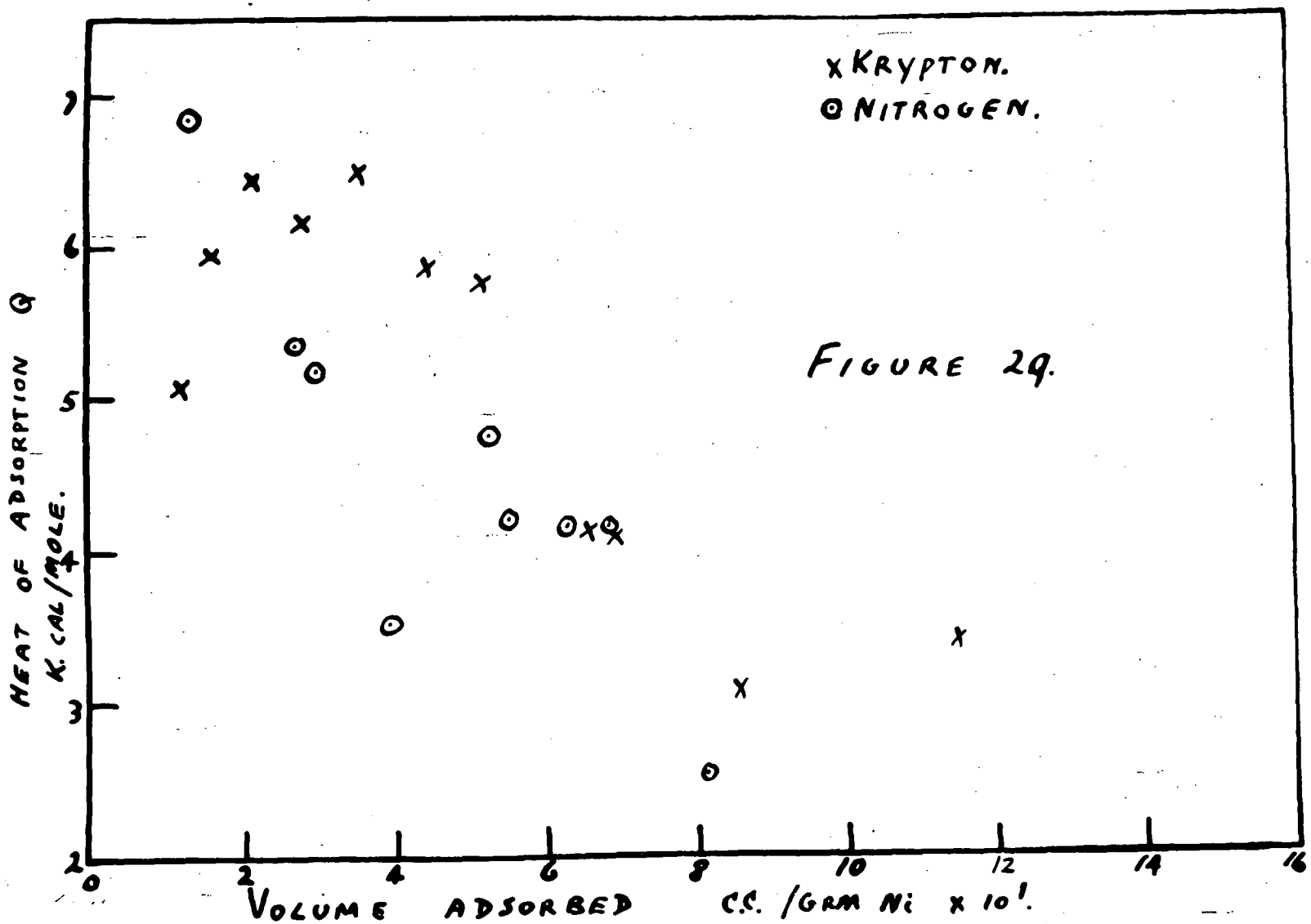

X KRYPTON.
O NITROGEN.
HEAT OF ADSORPTION Q
K. CAL/MOLE.
7
6
5
4
3
2
0
2
4
6
8
10
12
14
16
VOLUME ADSORBED C.C. /GRM Ni x 10¹.

FIGURE 29.

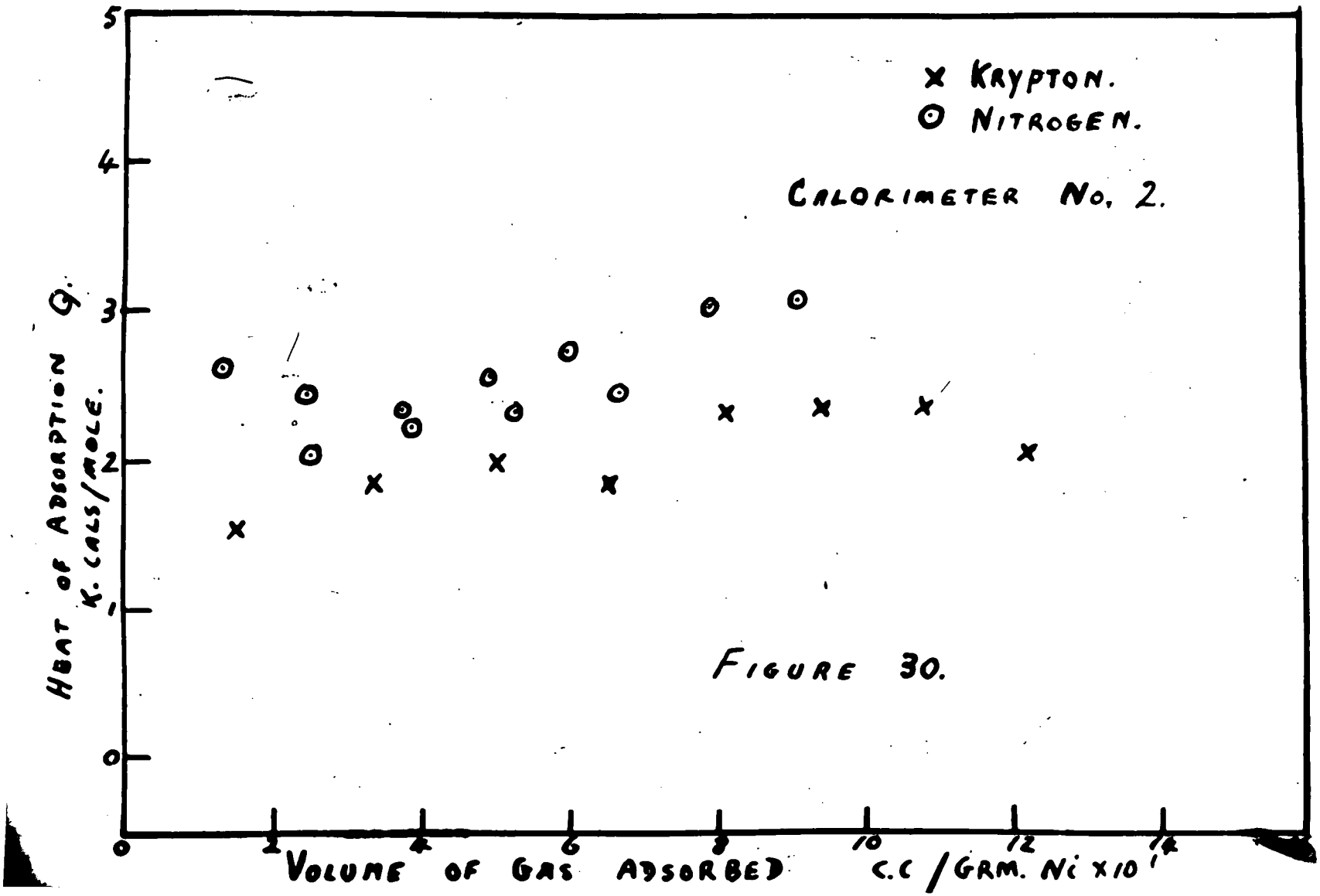

× KRYPTON.
⊙ NITROGEN.
CALORIMETER No. 2.
HEAT OF ADSORPTION Q.
K. CALS/MOLE.
VOLUME OF GAS ADSORBED C.C / GRM. Ni X 10
0
1
2
3
4
5
2
4
6
8
10
12

FIGURE 30.

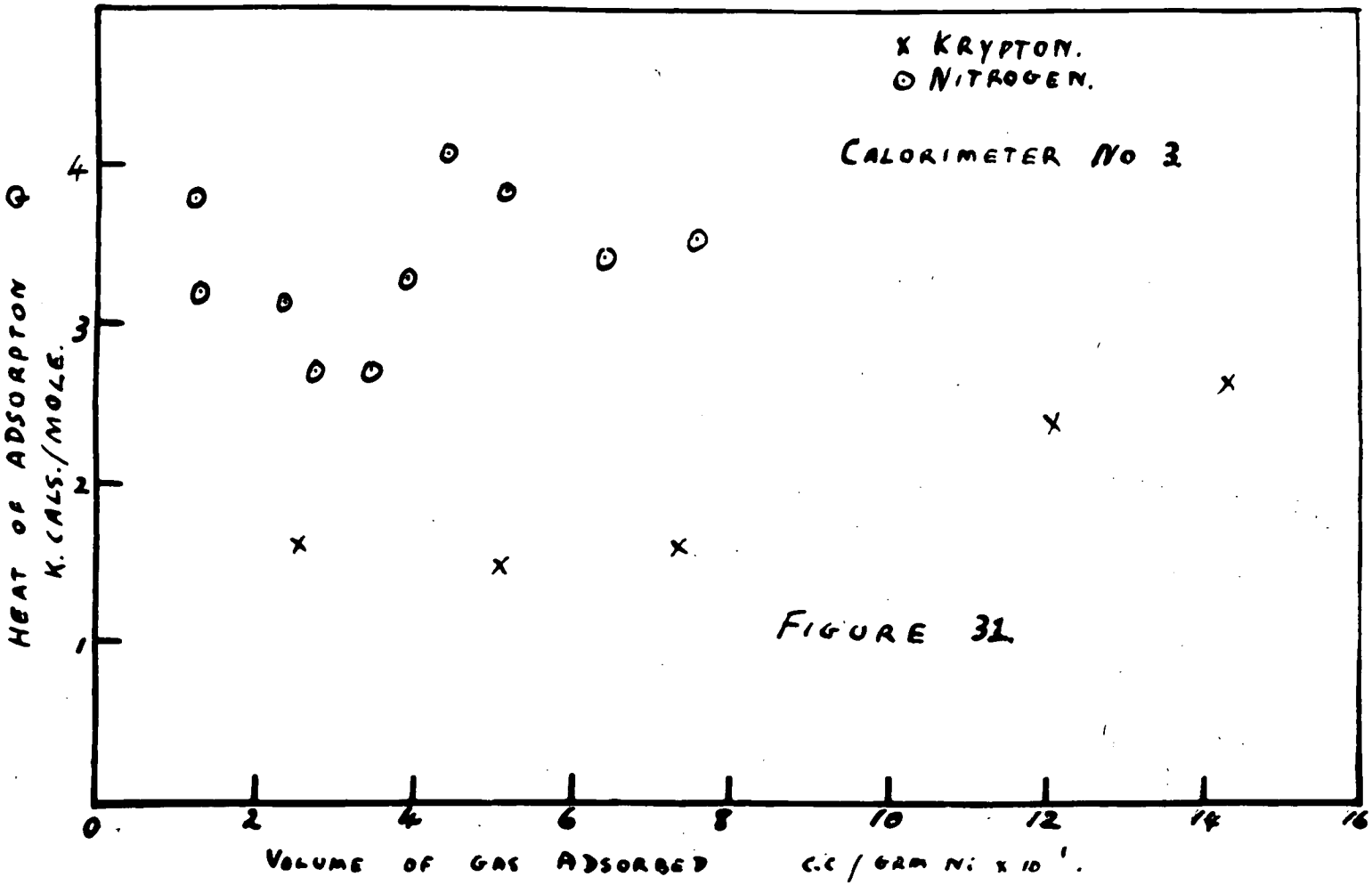

x KRYPTON.
⊙ NITROGEN.
CALORIMETER NO 3
Q
HEAT OF ADSORPTION
K. CALS./MOLE.
4
3
2
1
0
2
4
6
8
10
12
14
16
VOLUME OF GAS ADSORBED
C.C / GRM Ni x 10 ¹.

FIGURE 31.

reading this pressure (of the order of 0.5 cms.Hg.) would have a marked effect on the heat of adsorption values.

In an effort to improve this variation it was decided to include a large storage bulb of known capacity in the system. The bulb was filled with gas at a measured pressure and opened to the Pirani bulb. The storage bulb was of sufficient capacity so that the small volume of gas removed for each differential adsorption did not greatly effect the overall pressure. This meant that each differential adsorption would be at almost the same initial pressure. The actual pressure in the Pirani bulb prior to adsorption was checked against both the di butyl phthalate and the mercury manometers. This method was used in all measurements excluding those obtained with calorimeter No. 1.

Discussion of the Results of Calorimeter No. 1.

Examination of fig.(29) reveals the presence of a slight maximum. This is especially evident in the case of krypton. The explanation probably lies in -

1. Non uniform adsorption
2. Poor heat transfer.

With regard to non uniform adsorption it was appreciated that no provision had been made in the calorimeter design to assist gas distribution. It had been assumed that such a provision was unnecessary because of the loosely packed nature of the powder due to the contraction in volume during decomposition of the nickel oxalate.

If poor heat transfer is the explanation then the results should vary depending on the position of the platinum coil. It was decided to test this explanation by placing the platinum wire on the outside of the inner bulb and observing the effect. It was for this reason that calorimeter No. 2 was constructed and tested.

Discussion of the Results of Calorimeter No. 2

Table (II) and fig.(30) show several interesting features.

1. The spread of the results in duplicate measurements is much less than those obtained with calorimeter No.1. This indicates that inaccuracies in initial pressure measurements were in part at least responsible for the inconsistencies previously mentioned.

2. The overall values are considerably smaller (especially the first few points) than those obtained with calorimeter No. 1.

3. The values are approximately constant but there exists a definite tendency to increase, the larger the volume adsorbed.

4. The shape of the plots are in complete contrast with those generally accepted for physical adsorption.

The probable explanations of these results are:-

1. Poor thermal conduction through the glass walls of the inner bulb.

2. Poor heat transfer through the powder.

3. Non uniform adsorption due to the inability of the gas to penetrate easily and quickly to the bottom of the powder mass.

It was decided to test the third explanation by improving the gas distribution with a central inlet tube. Calorimeter No.3 was therefore constructed.

Discussion of the Results of Calorimeter No.3

The results shown in fig.(31) are very similar to those obtained with calorimeter No.2. This means that an improvement in gas distribution is of minor consequence in this type of calorimeter. This would suggest that the dominating factor is the poor thermal conductivity of the glass wall of the inner bulb.

General Conclusions

The results obtained with calorimeters No. 1, 2 and 3 are not good. No satisfactory differential heat measurements were obtained at -183°C. Of the three calorimeters tested No.1 was the most promising. An obvious improvement in design would be the inclusion of a perforated inlet tube to improve gas distribution. The design and testing of a calorimeter possessing this addition will be discussed in part II.

PART II

THE ADSORPTION OF GASES ON NICKEL OXIDE

INTRODUCTION

As mentioned in the introductory paragraph to this Section the aim of this investigation was to measure the differential heat of adsorption of oxygen and carbon monoxide on bulk nickel oxide at 20°C. Now the investigations described in Part I have indicated that non uniform adsorption of nitrogen at -183°C. on nickel powders plays an important role. It is doubtful if this effect could be completely eliminated in the the type of calorimeters designed.

Now from the results of Dell and Stone (106) on nickel oxide films, it was anticipated that each small addition of either oxygen or carbon monoxide on bulk nickel oxide would react with the upper layers of the powder whatever provisions were made for uniform gas distribution. It was decided, therefore, to restrict measurements to integral or average heat of adsorption rather than differential values.

Calorimeter No.4

This calorimeter, illustrated in fig.(32), was similar in design to No.1 but in addition possessed a central inlet tube. This inlet tube was perforated with a number of holes and loosely packed with glass wool to prevent blockage during outgassing and decomposition. The platinum leads entered the

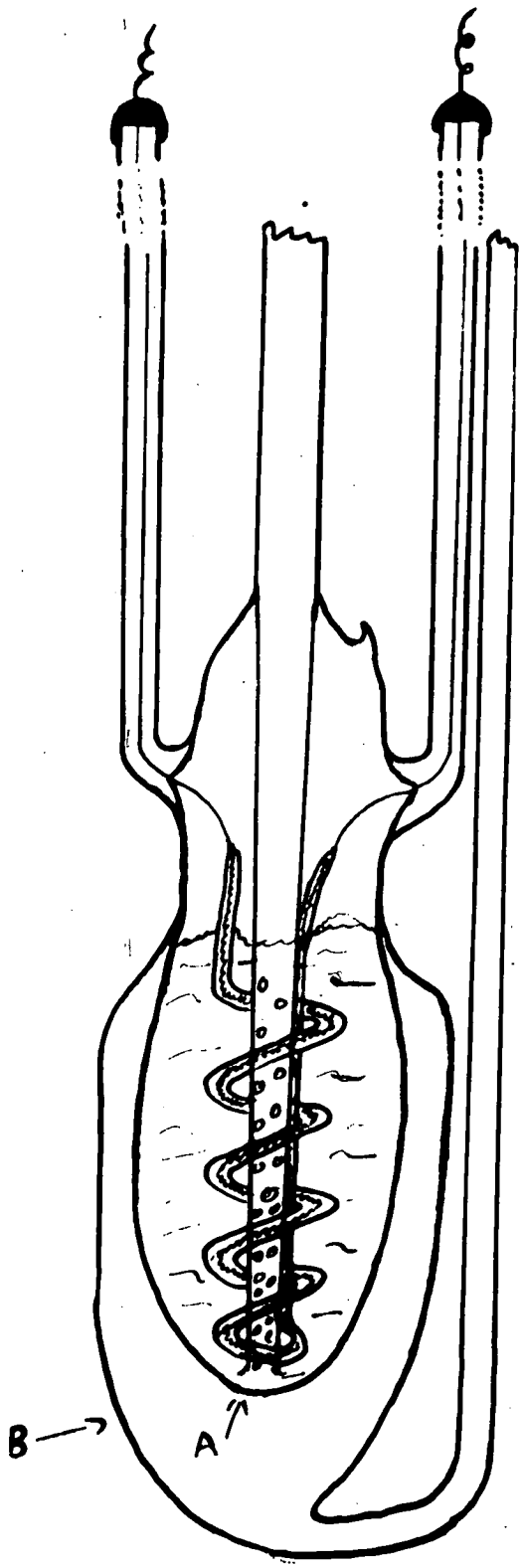


FIGURE 32.

calorimeter bulb by way of small diameter capillary tubing of sufficient length to allow the ends to remain clear of the liquid oxygen bath. With such an arrangement a satisfactory seal could be accomplished with apiezon black wax.

EXPERIMENTAL:

Reagents -

(a) Nickel Oxide:-

Bulk nickel oxide was prepared by the thermal decomposition of nickel hydroxide. The parent salt was prepared by treating a solution of reagent grade nickel nitrate with an excess of ammonia followed by steam distillation. This method has been shown to yield nickel hydroxide in a state of high purity (124). Teichner and Morrison (107) report that decomposition of nickel hydroxide at 210°C. is rapid, the product of decomposition having the composition $NiO.016H_2O$. However, continued heating of the product at 250°C. or higher at pressures of the order of 10^{-6} mm. Hg. led to a black oxide which had lines characteristic of metallic nickel in its x ray pattern.

In this investigation the nickel hydroxide (10 gms.) was placed in the calorimeter and decomposed at 230°C. However, several days continued decomposition were necessary before gas evolution fell off appreciably.

(b) Oxygen, Carbon Monoxide and Nitrogen:-

The preparation and purification of these gases has been described elsewhere in this thesis.

Apparatus

The apparatus used was identical to that described in Part I.

Procedure:

(a) Testing Calorimeter No. 4

The calorimeter containing nickel hydroxide was sealed in position and evacuated continuously for seventytwo hours at 230°C. When cold the calorimeter was immersed in a bath of liquid oxygen and after three hours the outside bulb continuously evacuated. Nitrogen was admitted in large doses so that the equilibrium pressure in the calorimeter could be measured with a mercury manometer. The temperature rise of the powder was recorded and from the known volume of the burette system the volume of nitrogen adsorbed was calculated.

(b) Oxygen and Carbon Monoxide Adsorption at 20° C.

The calorimeter containing the freshly prepared nickel oxide was placed in a large water bath maintained at room temperature (20°C.). The adsorption of both oxygen and carbon monoxide was then studied, the heat of adsorption being recorded. The gases were admitted, in most cases with evacuation at 20°C. in between admission in large amounts from the burette system so that the equilibrium pressures were measured with the mercury manometer.

The nickel oxide was evacuated at 200°C. and the measurements repeated. The measurements were also repeated

on fresh samples of nickel oxide.

RESULTS

(a) Testing Calorimeter No.4

The results of the heat of adsorption measurements of nitrogen at -183°C. on nickel oxide are given in Table (13) and plotted in fig.(33).

(b) The Adsorption of Oxygen and Carbon Monoxide on Nickel Oxide

These results have been divided into four groups given in Tables (14), (15), (16) and (17).

Table (14) gives the results of successive additions of oxygen, to the pressure listed, with intervening evacuations where indicated.

Table (15) gives the results of similar experiments with carbon monoxide.

Table (16) shows the consequence of adding successively oxygen, carbon monoxide and then oxygen, with intervening evacuations as indicated.

The final results given in Table (17) are for the sequence carbon monoxide, oxygen and carbon monoxide.

TABLE (13)

TESTING CALORIMETER NO.4

Wt. nickel oxide = 9.51 gms.

Surface area = 140 m^2/gm.

Total Volume N_2 Adsorbed cms.^{3} S.T.P./Gm.	Heat of adsorption K cals./mole.
2.82	2.71
8.65	1.98
13.72	1.81
19.77	1.73
23.01	1.70
28.24	1.51
32.66	1.25

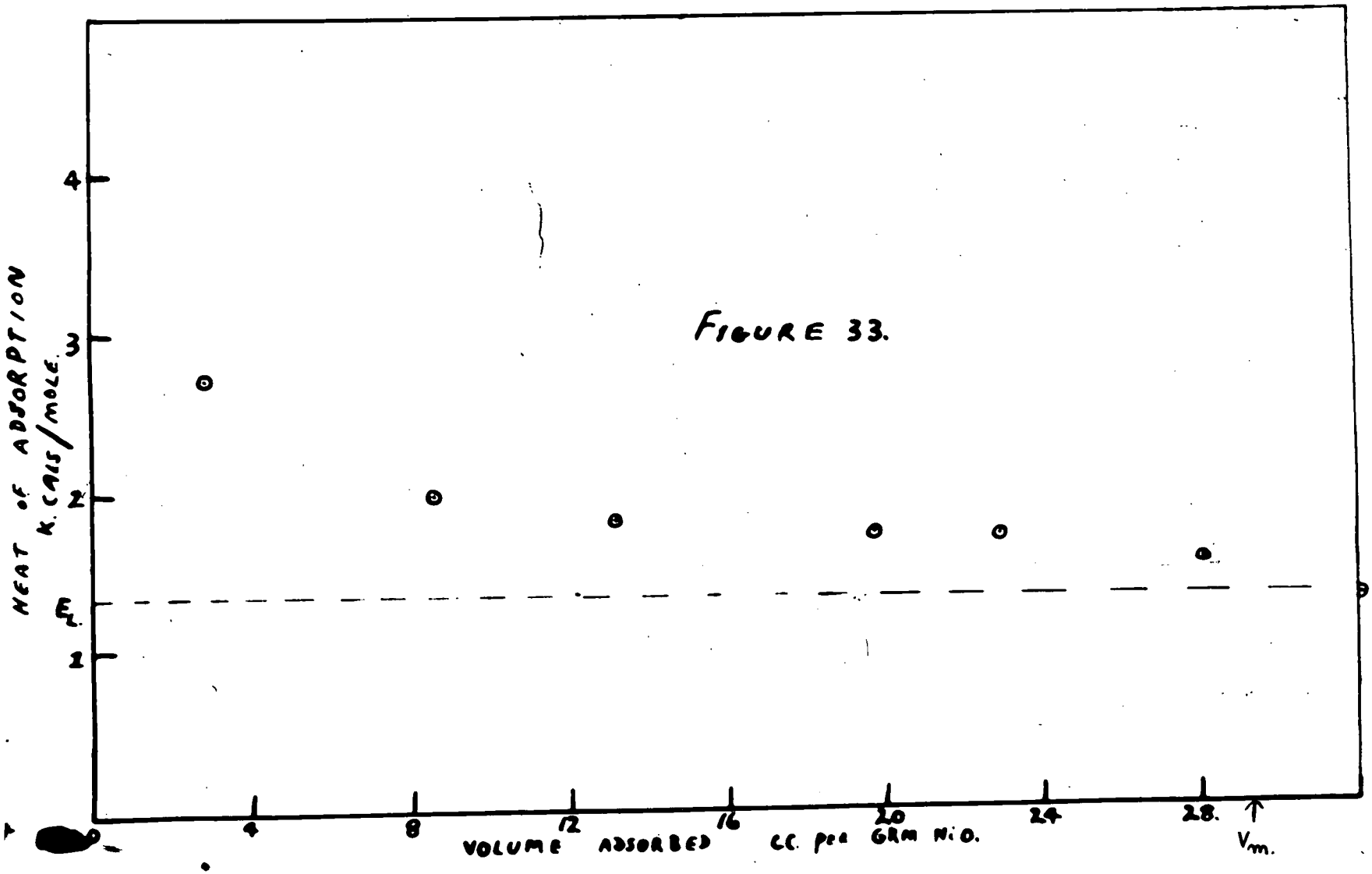

HEAT OF ADSORPTION
K. CALS/MOLE.
4
3
2
E
2
0
4
8
12
16
20
24
28.
Vm.
VOLUME ADSORBED CC. per GRM Ni O.

FIGURE 33.

TABLE (14)

Wt. Ni0 = 9.51 gms. S.A. = 140 m^2/gm.

Step	Press. after 10 mins. cms. Hg.	Volume O_2 ($cms.^3$ S.T.P.)	ΔH. K.cals./mole
1.	Decomposition of $Ni(OH)_2$ at 230°C.		
2.	3.36	0.66	9.5
3.	6.01	0.35	4.8
4.	10.38	0.47	4.9
5.	15.81	0.51	4.8
6.	Evacuation at 20°C. overnight.		
7.	3.66	0.32	4.6
8.	6.60	0.28	4.6
9.	Evacuation at 200°C. for 2 hours.		
10.	3.74	0.32	4.8
11.	Evacuation at 200°C. for 6 hours.		
12.	3.72	0.39	5.5
13.	Evacuation at 360°C. for 48 hours.		
14.	2.94	0.125	17.78

TABLE (15)

Wt.NiO = 9.51 gms. S.A. = 140 m^2/gms.

Step	Pressure after 10 min. cms.Hg.	Volume CO ($cms.^3$ S.T.P.)	ΔH K.cals./mole.
1. Evacuation of NiO at 230°C. for 16 hours.			
2.	0.06	3.31	52.9
3.	0.13	2.32	38.6
4.	0.21	3.29	35.5
5. Evacuation at 20°C. for 12 hours.			
6.	0.14	4.11	36.2
7.	0.65	4.61	30.2
8.	1.63	6.25	17.2
9.	3.14	3.49	8.34

TABLE (16)

Wt.NiO = 9.51 gms. S.A. = 140 m^2/gm.

Step	Press. after 10 min. cms. Hg.	Volume ($cm.^3$ S.T.P.) CO	Volume ($cm.^3$ S.T.P.) O_2	ΔH K. cals./mole.
1.	Evacuation of NiO at 360°C. for 48 hours.			
2.	2.94	-	.125	17.78
3.	Evacuation at 20°C. for 12 hours.			
4.	3.85	-	.23	5.4
5.	Evacuation at 20°C. for 1 hour.			
6.	0.16	4.07	-	52.9
7.	0.74	4.93	-	24.6
8.	2.47	2.65	-	13.08
9.	Evacuation at 20°C. for 12 hours.			
10.	2.33	-	1.85	35.6
11.	4.41	-	0.16	8.9

TABLE (17)

Wt. NiO = 9.51 gms. S.A. = 140 m^2/gm.

Step	Press. after 10 min. cms. Hg.	Volume (cm^3 S.T.P.) CO	Volume (cm^3 S.T.P.) O_2	ΔH K. cals./mole
1	Evacuation of NiO at 200°C. for 12 hours.			
2	0.06	3.31	-	52.9
3	0.13	2.64	-	27.2
4	0.92	3.34	-	17.8
5	Evacuation at 20°C. for 12 hours.			
6	1.10	-	2.87	41.3
7	Evacuation at 20°C. for 1 hour.			
8	5.38	-	0.45	6.33
9	Evacuation at 20°C. for 1 hour.			
10	0.32	3.69	-	29.2

DISCUSSION

(a) Testing Calorimeter No. 4

It is difficult to compare the results given in Table (14) and fig.(33) because of the absence of suitable published data. Most investigations on heats of adsorption have been confined to evaporated metal films. Following a suggestion by Beeck (113) these films are supposed to be completely covered at a pressure of 0.1 m.m.Hg. and all measurements have been confined to pressures below this figure (113)(123) (125). In all such cases the values fall from initial high values at low coverage to approach the heat of liquifaction E as the coverage $\longrightarrow 1$.

In regard to powdered materials Beebe and co-workers (117) have studied various adsorbents but not nickel oxide. In all these investigations, however, the heats of adsorption fall to approach E as $\frac{V}{V_m} \longrightarrow 1$. Trapnell (126) has recently compared results for powdered metals and evaporated films and has noted that the powdered results are invariably lower.

The nearest approach to the present work is that of Kingston and Aston (127) on the adsorption of nitrogen on anatase at $-195^{\circ}C$. They found that the heat of adsorption fell from 5 K cals./mole. down to a value close to E at $\frac{V}{V_m} = 1.5$

In the present investigation, it should be noted that the values are integral and not differential heats of adsorption

and are therefore lower. It may be seen from fig.(33) that the values approach the value of E as $V \rightarrow V_m$.

The fact that values of the right order were obtained indicates that the calorimeter was satisfactory in its operation at -183°C.

Oxygen and Carbon Monoxide Adsorption

Before discussing the results in detail a few general points may be made.

1. The majority of both the oxygen and carbon monoxide admitted to the oxide at 20°C. was adsorbed rapidly but in each case there was a smaller slow uptake extending over several hours. The carbon monoxide adsorption was somewhat slower than that of oxygen. The pressures listed in the Tables are those recorded after ten minutes adsorption and do not represent equilibrium values. Heat of adsorption readings were taken for ten minues andafter this time the pressure was measured in order to calculate the volume of gas adsorbed up to this time, a figure necessary in evaluating the ΔH values.

2. Carbon monoxide was adsorbed to a much greater extent than was oxygen. This is in contrast to the results of Bell and Stone (106) on nickel oxide films but in general agreement with Teichner and Morrison (107).

3. The nickel oxide contaminated by several

adsorptions could be regenerated by heating in vacuo at 200°C. This observation is in accord with the results of Teichner and Morrison. However the extent of regeneration was found to be dependent on both the time and temperature of evacuation.

DETAILED DISCUSSION

(a) Oxygen Adsorption

The results given in Table (14) possess several interesting features.

1. The integral heat of adsorption of the first oxygen admitted is 9.5 K cals./mole, which may be compared with a value of 43 K cals./mole found by Dell and Stone (106). This lower value was, however, expected because in the case of nickel oxide films there is almost certainly some reaction between the adsorbed gas and the underlying nickel metal. This suggestion is confirmed by an observation made during the kinetic studies described in Section III. It was noted that nickel powders supposedly saturated with oxygen at 300°C. after some days standing in vacuo, reacted with further oxygen at room temperature. Presumably, during evacuation fresh nickel metal became exposed.

This explanation is confirmed by steps 13 and 14 in Table (14). Teichner and Morrison (107) have noted the appearance of metallic nickel when the bulk oxide was evacuated at temperatures above 250°C. Presumably in step

13 this occurred so that when oxygen was admitted in step 14 the nickel was oxidized giving rise to a higher integral heat of adsorption.

2. The effect of time on the regeneration of the oxide by evacuation at 200°C. is shown in steps 9 - 13 in Table (14). Owing to the large mass of oxide used (≃ 10 gms.) it was difficult to completely remove adsorbed gas even with evacuation overnight.

3. It is difficult to compare the volume of oxygen adsorbed with the results of Teichner and Morrison because these authors failed to record the equilibrium pressures. They state that each gas was adsorbed to saturation.

In the present investigation the adsorption of oxygen was studied up to an equilibrium pressure of 40 cms.Hg., but this was not the saturation pressure. The values have not been given in detail as they do not conform to any of the well known isotherms. The magnitude of the effect of pressure on the volume of oxygen adsorbed at 20°C. can be gauged, however, from steps 1 - 5 in Table (14). It must be realised, however, that the pressures listed are those measured after ten minutes adsorption and are somewhat higher than the equilibrium values.

(b) Carbon Monoxide Adsorption

The rapid adsorption of carbon monoxide giving an integral heat of 53 K cals./mole was reproducible to 1%.

However, the heat evolved in the slow reaction (extending over several hours as judged by the pressure drop) was difficult to evaluate. This slow exothermic reaction slowed down the normal rate of cooling. Thus the galvanometer plots were flatter than those usually obtained and hence the extropolated values and, therefore, the heats of adsorption are lower than would be expected in the absence of this secondary reaction. The values of 36 K.cals./mole. found for latter additions are probably low because of this factor.

The value of 53 K.cals./mole is double the value found by Dell and Stone (106).

(c) Sequence -Oxygen, Carbon Monoxide Oxygen

The results obtained for this sequence are in contrast to those found by Dell and Stone (106).

1. The second lot of oxygen (step 10 Table (16)) was adsorbed with a heat of 36 K.cals./mole. which is considerably larger than that found for the first adsorption. Dell and Stone (106) found, however, similar values (43 K.cals./mole.)

2. The heat of adsorption of carbon monoxide is the same (53 K.cals./mole.) whether the oxide is clean or presaturated with oxygen. This is in contrast to Dell and Stone who found a higher value for the presaturated with oxygen run. The present results seem more likely because it has been shown (107) (112) that freshly prepared nickel oxide

contains an excess of oxygen. Therefore the conditions with regard to the presence of oxygen are the same in either case.

In the case of nickel oxide films on underlying nickel metal, when freshly prepared, any excess oxygen would react with the underlying nickel. Therefore the conditions, at least in regard to the presence of adsorbed oxygen, would be different in the two cases and hence the difference in the heat of adsorption of carbon monoxide observed by Dell and Stone is not surprising.

(d) Sequence - Carbon Monoxide, Oxygen, Carbon Monoxide

The results are again different in magnitude to those found for oxide films but certain features are common, thus

1. The heat of adsorption of oxygen on the oxide saturated with carbon monoxide is considerably higher than on the clean surface. This same effect was noted by Dell and Stone (106).

2. A further lot of carbon monoxide could be adsorbed (step 10 Table (17)) as the result of adsorption of oxygen on the oxide saturated with carbon monoxide. The heat evolved, however, was less than previously found and possibly is in error owing to the secondary slow reaction discussed previously.

GENERAL DISCUSSION

The results of this investigation while at variance with some findings of Dell and Stone (106) substantially support the work of Teichner and Morrison (107). However, in the absence of equilibrium pressures in the latter publication a complete comparision is impossible.

The present work has shown that the adsorption at 20°C. is a function of the pressure. This finding is in agreement with the work of Engell and Hauffe (111), but would appear to be contrary to the work of Teichner and Morrison who mention adsorption up to saturation. In the present investigation no saturation was observed up to an oxygen pressure of 40 cms. Hg.

The inability to thoroughly out-gas the large mass of powder used in this investigation may be an explanation of the fact that the volumes of gases adsorbed were smaller than those previously reported (107). However, the lack of equilibrium pressures confuses this issue. It may be noted, however, that the present results are more in accord with the work of Krauss (112) than are those of Teichner and Morrison (107).

The present investigation has confirmed the findings of Engell and Hauffe (111) that two rate processes are involved in the adsorption of oxygen and carbon monoxide.

However, in both cases the heat associated with the fast reaction only was measured.

Although the present results differ somewhat in magnitude from those of Teichner and Morrison (107) there are two features in common:-

(1) Carbon monoxide is adsorbed to a greater extent than is oxygen.

(2) Both oxygen and carbon monoxide can be removed and the oxide regenerated by evacuation at 200°C. Both these findings are in contrast to the results of Dell and Stone (106) on nickel oxide films. An explanation might be the probable presence of metallic nickel in the oxide films. This could also explain the differences found in the heats of adsorption.

With regard to the regeneration of the oxide by evacuation at 200°C. it is doubtful if the carbon monoxide adsorbed with a heat of 53 K.cals./mole. would be removed at this temperature. This is supported by the fact that regeneration was slow at 200°C. but enhanced at higher temperatures. It is probable that at 200°C. or higher the carbon monoxide may enter the bulk of the oxide, thus effectively regenerating the surface. This aspect requires further investigation before definite conclusions can be made.

Dell and Stone (106) suggest the formation of a complex of the type CO_3, but this is challenged by the work of Teichner and Morrison (107). The present investigation would tend to support the contention that a complex exists, but direct proof as to the formulae is not available.

A criticism of the present work is that the nickel oxide could not be completely outgassed at 200°C. Such a criticism can, however, be levelled at all investigations involving powdered materials, whatever the temperature of out-gassing.

A further criticism is the non-inclusion of a liquid air trap between the adsorbent and the burette system.

Owing to the particular design of the apparatus used the inclusion of such a trap was impossible and therefore the present results may have been affected by the presence of mercury vapour.

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